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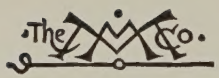

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REFERENCE BOOK

OF

INORGANIC CHEMISTRY

BY

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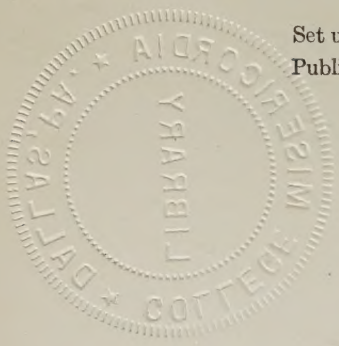

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PREFACE

This book represents the fulfillment of a plan, long cherished, of providing a volume of descriptive chemistry to complete the series begun with "Principles of Chemistry" by Hildebrand, which adheres strictly to its title, and continued with the "Course in General Chemistry" by Bray and Latimer, which presents a laboratory course. The rather radical experiment in teaching general chemistry, begun in the University of California in 1912, has been somewhat hampered by the lack of a reference book on descriptive chemistry employing the language and the point of view adopted for our instructional scheme.

This "Reference Book of Inorganic Chemistry" has been written as a reference book rather than a text. The authors have sought to present essential chemical facts briefly, clearly, and in due relation to other facts and principles. The instructor using it will have to map out his own course, following whatever order of arrangement appeals to him. The numbering of paragraphs will make it possible for him to assign for study material selected from any desired portion of the book. We feel that many teachers will welcome the greater freedom thus afforded of developing their own pedagogical methods.

Chemical properties have been widely related to atomic structures and sizes. These ideas, although new, and subject to revision, are so illuminating that they appeal strongly to the imagination. Moreover, they are not difficult to grasp; many concepts traditionally introduced into freshman courses are far more elusive.

The formulas of many compounds have been given in terms of the Lewis theory of valence, not with the idea that these formulas represent the definite locations of the electrons, but rather to call attention to the importance of considering the total number of electrons or electron pairs in a molecule.

The extensive tabulation of "half reaction" potentials, equivalent to free energy values, will enable one to predict the direction and driving force of an immense number of reactions. Many of these potentials have been calculated for this book from reaction heats and entropy values, and have not heretofore been published.

We have treated industrial processes with emphasis upon their chemistry, relation to other industries, and economic magnitude,

6017

rather than upon their mechanical features. Illustrations of industrial processes, of the sort extensively used in some texts, have been left to the instructor to provide, as he can do so far more adequately, by the use of lantern slides and motion pictures. Many excellent films are now available at a nominal expense.

The book contains much more material than the average student, or even the average chemist, can assimilate. We believe, however, that students should be "exposed" to a far greater range of subject matter than is usually presented. We have found the appetite and assimilative capacity of the superior students to be almost unlimited, and we see no value in an intellectual diet list. For the average student, the presence of this extra material in the book does no more damage than the unordered articles listed on a restaurant menu.

We anticipate that this kind of a book will prove useful, not only to the freshman student, but also to the student who desires a reference book in advanced courses in chemistry and allied subjects; and further that teachers and industrial chemists will also find in it answers to many of their questions. To increase its usefulness, a large mass of data has been included in the form of tables, both in the text and in the various appendices.

In the endeavor to keep the size and cost of the book at a low figure, it was decided to omit references to the original sources of material, although in many instances such references would be of historical and scientific value. Frequent use has been made of the more comprehensive treatises, especially: Gmelin-Kraut's Handbuch der anorganischen Chemie; Abegg and Auerbach Handbuch der anorganischen Chemie; A Text-Book of Inorganic Chemistry, Edited by Friend; A Comprehensive Treatise on Inorganic and Theoretical Chemistry by Mellor; Lexikon der anorganischen Verbindungen by Hoffman; Landolt-Börnstein Tabellen; and The International Critical Tables.

The authors are much indebted to their colleagues in the Department of Chemistry of the University of California, especially to Professors G. N. Lewis and W. C. Bray, not only for specific criticisms and suggestions, but for many of the general ideas upon which our interpretation of the facts of inorganic chemistry has been constructed.

Wendell M. Latimer
Joel H. Hildebrand

Berkeley, California
December, 1928.

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CHAPTER I

HYDROGEN

1. Structure of Hydrogen Atom.—The hydrogen atom is a system composed of two corpuscles; one, the proton, is the unit charge of positive electricity and the other, the electron, is the unit charge of negative electricity. The mass of the proton is about 1,850 times that of the electron but the electrical charges, though opposite in sign, are equal in magnitude.

The atom has a large number of energy states representing different configurations of the electron and proton. The values for the energy of the atom in these different states may be expressed as a close approximation by the very simple relation, $E = \frac{-13.54Z^2}{N^2}$ volts per unit charge, where Z is the charge on the proton (equal to unity) and N, called the **quantum number,** is any integer from 1 to ∞. The normal atom is in the first quantum state ($N = 1$) and the energy in volts required to move the electron to the 2, 3, 4, 5, $\cdots$ ∞ quantum states is shown in Figure 1. When $N = \infty$ the energy is zero. This corresponds to the complete separation of the electron and proton, and the total energy required per unit charge is given as 13.54 volts.

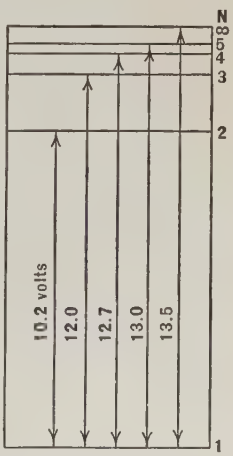


FIG. 1.—Energy levels in the hydrogen atom.

When the electron moves from a higher quantum level to a lower, the energy difference is emitted in the form of light, whose frequency, ν, is related to the energy difference, ΔE, by the equation, $\Delta E = h\nu$, where h is a constant ("Planck constant"). Likewise the atom in a lower quantum state may absorb energy in the form of light of a

given frequency and the electron thereby move to a quantum level of correspondingly higher energy. The spectral lines arising from electrons falling from outer levels to the first quantum level are far out in the ultraviolet, but transitions from outer levels to the second quantum state give rise to the Balmer series which is in the visible spectrum. The highest frequency in the hydrogen spectrum is, of course, that corresponding to the electron falling from the infinite quantum state.

Bohr has sought to account for these quantum states by picturing the electron as revolving about the proton in some one of a number of possible orbits, which are circles or ellipses. These orbits are defined by the restriction that the momentum of the system must always be some multiple, i.e. the quantum number, of a single fundamental quantity. The total quantum number is made up of two factors, $N = N_A + N_R$, the one, N_A, determining the angular momentum and the other, N_R, the radial momentum, that is, momentum in the direction of the radius. These numbers fix the size of the orbits and also the ratio of the major (a) and semi-minor (b) axes of the orbits. The semi-major axis of the orbit is given by $a = \frac{0.53N^2}{Z} 10^{-8}$ cm. For $N = 1$, the stable state of the atom, this gives $a = 0.53 \cdot 10^{-8}$ cm. When $N_R = 0$, the orbits are ellipses whose major and minor axes are in the ratio N/N_A.

Figure 2 represents these orbits for $N = 1$, 2, and 3. The large numbers give the values of N, the subscripts the values of N_A. While the existence of discrete energy states has been well established, we cannot regard the Bohr picture as entirely exact. Later developments by Schrödinger and others have generalized the quantum mechanics and modified somewhat Bohr's assumptions, but, as yet, they have given no detailed physical picture of the atom.

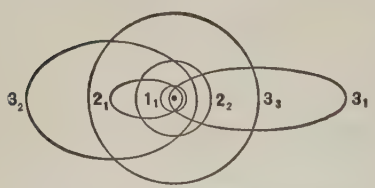


Fig. 2.—Electron orbits of hydrogen as pictured by Bohr.

2. The same general quantum relations as outlined above hold for the other elements, complicated, however, by the facts: (1) that the positive center is no longer a simple unit charge but a complex structure with a net positive charge equal to the

atomic number, and (2) that the number of electrons is not one, but a number equal to the atomic number. It is the distribution of these electrons among the various quantum states that determines the grouping of the elements into the so-called "chemical families." The maximum number of electrons in any atom that can have the same total quantum number N is $2N^2$, e.g. for $N = 1$, the maximum number of electrons is 2; for $N = 2$, it is 8. Hence when the first quantum level is complete with the second element, helium, the three electrons of the third element, lithium, cannot all remain in the first level, but one of them is forced into the second. With each succeeding element of higher atomic number, the number of electrons in the second level increases until it is filled with eight electrons, i.e. in neon. Each alkali metal marks the beginning of a new quantum group and each noble gas the completion of a group. A complete table of the distribution of the electrons for all the elements is given in the appendix.

3. Occurrence of Hydrogen.—Only about one per cent by weight of the earth's crust (outer 10 miles) is hydrogen. However, if the composition is expressed in terms of the number of atoms, it may be stated that about sixteen per cent of all the atoms on the earth's surface are hydrogen, being second in abundance to oxygen. The major portion of the earth's hydrogen is combined with oxygen in water. It also frequently occurs combined with sulfur, carbon, nitrogen, and chlorine, and less frequently with the other halogens and phosphorus. Hydrogen is a constituent of all acids, and of all animal and vegetable tissue. Only a trace of free hydrogen is found in the atmosphere, about 1×10^{-3} per cent by volume. Larger quantities are sometimes found in volcanic and other natural gases. The spectrum of the sun indicates that enormous flames of incandescent hydrogen are frequently shot out distances of thousands of miles.

4. Molecular Hydrogen.—Atomic hydrogen combines to form the molecule H_2. Representing the proton by **H**, and the electron by a dot, we may write **H:H** as the electronic formula of the molecule. The exact arrangement of the charges in the molecule is not known so that the formula as written simply indicates that the two electrons constitute a bond holding the two protons together. The heat of formation is large, about 100,000 calories (100 kg. cal.). At temperatures of the electric arc, the molecule

is dissociated to a considerable extent into the atoms. In the absence of a catalyst the rate of combination of the atoms to form the molecule is slow.

Hydrogen has the lowest molecular weight and hence the smallest density of any substance, and, with the exception of helium, the lowest melting point and the lowest boiling point. The gas is odorless, tasteless, and colorless. The more important physical constants are collected in Table I.

TABLE I

PHYSICAL CONSTANTS OF HYDROGEN

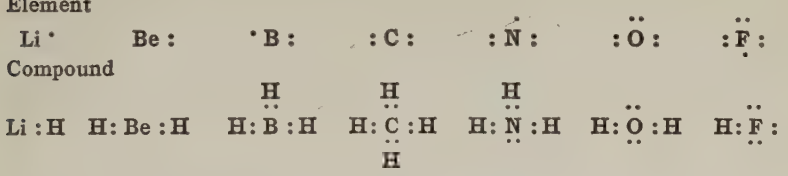
Melting point, ° C.	− 259.2	Density g./liter at 0° and 760 mm.	0.08985
° A.	13.9		
Heat of fusion, cals. per mole	15	Density of liquid g./cc.	0.071
Boiling point, ° C.	− 252.7	Solubility in water at 25° vol. per 100 vol. of H_2O	1.8
° A.	20.4		
Heat of vaporization, cals. per mole	218	Equilibrium constant for dissociation, $H_2 = 2H$. At 2,000°	3×10^{-4}
Critical temperature, ° C.	− 241	3,500°	3.8
° A.	32		
Critical pressure, atmos.	20		

Hydrogen was first liquefied by Dewar (1898). The gas in expanding from high pressure to low pressure is heated at ordinary temperatures, but if cooled in liquid air (− 185° C.), the sign of this heat is reversed. Advantage is taken of this fact in the liquefaction process. (For further discussion of liquefaction process cf. **III—6**). The metals of the nickel, palladium, platinum groups occlude or dissolve hydrogen to a remarkable degree. Under certain conditions one volume of palladium will take up almost 900 volumes of hydrogen at 20° and 1 atmosphere. (Cf. Palladium, **XX—27**.) Molecular hydrogen has a very high relative rate of diffusion since this property is inversely proportional to the square root of the density. Thus the densities of hydrogen and oxygen are in the ratio of 1/16 and hydrogen diffuses four times as fast as oxygen.

5. Reactions of Hydrogen.—Hydrogen combines directly with most of the lighter elements, accompanied in the case of the

more electronegative elements with the evolution of large amount of energy; e.g. a jet of hydrogen burns readily in an atmosphere of oxygen or chlorine, and its mixtures with these gases are highly explosive.

The electron formulas of the compounds with the elements from lithium to fluorine are as follows:



The more negative the element, the more completely does it tend to acquire the electrons of hydrogen, thus leaving the hydrogen with a valence of + 1. The more positive elements, on the other hand, tend to lose their electrons to hydrogen, giving it a valence of − 1, since, as mentioned in Paragraph 2, there is room for two electrons in the first quantum state of the hydrogen atom. In this respect hydrogen resembles the halogen family, all members of which lack one electron of completing the noble gas structure. The details of the reactions of hydrogen will be discussed under the various elements, although the general reaction of hydrogen to hydrogen ion is to be considered under the following topic.

6. Properties of the Hydrogen Ion.—Hydrogen ion is the substance present in all solutions of strong acids and its properties are the familiar properties common to all acids, such as sour taste, characteristic color changes with organic indicators, e.g. the change of blue litmus to red, the neutralization of bases and the solution of base metals. A complete statement of the properties of hydrogen ion would include values for the degree of dissociation, volatility, and solubility of all of its compounds, since these quantities determine the extent to which hydrogen ion will unite with negative ions. For example, the statement that the concentrations of hydrogen ion and hydroxide ion in pure water are 10^{-7} moles per liter is equivalent to saying that the reaction, $H^+ + OH^- = H_2O$, takes place until the concentrations of the ions reach this value. Likewise the statement that the volatility of hydrogen chloride from its water solution

is high at 100° C. is equivalent to saying that the reaction, $H^+ + Cl^- = HCl$ (gas), has a strong tendency to take place at this temperature.

7. Many of the most important reactions of hydrogen ion and hydrogen gas may be summarized in terms of the oxidation-reduction couple, $\frac{1}{2}H_2 = H^+ + E^-$. (The electron will be denoted by a dot in certain structural formulas, as in Paragraph **3**, but in writing ordinary equations, we will use the symbol E^-.) For example, zinc will displace or liberate hydrogen from acids because the reaction, $Zn = Zn^{++} + 2E^-$, gives a higher "pressure" (voltage) of electrons. The total reaction, $Zn + 2H^+ = Zn^{++} + H_2$, is the result of the transfer of the electrons from the zinc to the hydrogen ion. On the other hand, the reaction $Ag = Ag^+ + E^-$ has a lower voltage than hydrogen; and hydrogen reduces silver ion, $2Ag^+ + H_2 = 2Ag + 2H^+$, by the transfer of electrons from the hydrogen to the silver ion. Reference may be made to the table of oxidation-reduction potentials (Append. II) for the position of hydrogen in respect to a large number of oxidation-reduction couples. Mention should be made of the fact that the oxidation of metals by hydrogen ion is often a slow reaction, and that the speed depends greatly upon the nature of the surface upon which the gas deposits. Thus the action of acid upon zinc proceeds very slowly if the zinc is pure, and rapidly only when impurities are present. The power of hydrogen ion as an oxidizing agent depends, of course, upon its concentration. In normal alkaline solution, a stronger reducing agent is required to liberate hydrogen than in acid since the potential of the reaction, $\frac{1}{2}H_2 + OH^- = H_2O + E^-$, is 0.83 volts more positive than the potential of the acid couple.

Although the formula of hydrogen ion in water solution is written as H^+, the ion exerts such a strong attraction upon the water molecules that it might be written $H(H_2O)_n^+$. The energy of hydration of the hydrogen ion, approximately 250,000 cal., is larger than that of any other singly charged ion.

8. Preparation.—Although hydrogen is liberated by the action of the electropositive metals, such as sodium, potassium, and calcium upon water, these metals are too expensive for its practical preparation. Hydrogen is sometimes prepared by passing steam over finely divided iron heated to redness. $3Fe + 4H_2O = Fe_3O_4 + 4H_2$. The gas is conveniently prepared in

the laboratory by the action of dilute sulfuric or hydrochloric acid upon zinc or aluminum. Hydrogen so prepared usually contains small quantities of volatile hydrogen compounds resulting from the presence of impurities in the metals. These may be removed by bubbling the gas through a permanganate solution. Water vapor is conveniently removed by contact with concentrated sulfuric acid.

There are three principal sources of commercial hydrogen: the reduction of water by carbon, the destructive distillation of coal, and the electrolysis of aqueous solutions. The reduction of water by carbon involves the water gas reaction: $H_2O + C = CO + H_2$, and the further reaction, $H_2O + CO = H_2 + CO_2$ (cf. **XIII—6**). Coke-oven hydrogen is a by-product of the destructive distillation of coal and contains large quantities of methane, CH_4, which may be removed by liquefaction. Electrolytic hydrogen is now usually prepared by the electrolysis of concentrated sodium hydroxide solutions with iron or nickel electrodes. Hydrogen is liberated at the cathode and oxygen at the anode. The gas is quite pure except for a small quantity of oxygen which is present by diffusion from the anode. This may be removed by passing the gas over a catalyst, e.g. finely divided nickel at 250° C., which accelerates the combinations of hydrogen and oxygen. Large quantities of hydrogen are also formed as a by-product in the manufacture of sodium hydroxide (cf. **IV—12**) by the electrolysis of salt brine.

9. Commercial Uses.—The oxy-hydrogen flame is used in cutting and welding metals. The temperature of the flame is approximately 2,500° C. A special burner is employed which prevents the explosion of the gases by mixing them just before they reach the orifice. The atomic hydrogen torch, recently developed, has many advantages in welding under reducing conditions. The atomic hydrogen is formed by blowing hydrogen through a very hot electric arc. The metal surface acts as a catalyst for the union of the atomic hydrogen and is heated to a high temperature, estimated between 4000 and 5000° C, by the heat liberated through the formation of the H_2 molecule.

Large quantities of hydrogen are consumed in the manufacture of synthetic ammonia by the direct union of the elements. The synthetic production of methanol, CH_3OH, and other liquid fuels by the reaction of hydrogen and carbon monoxide in the

presence of catalysts promises to become of great industrial significance. Another important use is in the hydrogenation of many oils, such as cotton-seed oil, to form solid fats.

Hydrogen is also employed as a lifting medium in balloons. Its efficiency depends upon the difference in weight of equal volumes of hydrogen and air. This is 1.2 grams per liter at 0° C. and 1 atmosphere.

10. Analytical.—Hydrogen is often determined by mixing with an excess of oxygen and passing the mixture over a glowing filament electrically heated. The per cent of hydrogen is calculated by the contraction in volume due to the formation of water. Hydrogen is also determined by passing the gas over hot copper oxide, $CuO + H_2 = Cu + H_2O$, and absorbing the water in a weighed tube of calcium chloride.

CHAPTER II

INERT GASES: HELIUM, NEON, ARGON, KRYPTON, XENON, RADON

1. As early as 1784, Cavendish showed that air contained a small amount of an unknown gas which was quite non-reactive, but further work on the subject was not published until 1893, when Lord Rayleigh found that the weight of 1 liter of nitrogen prepared from pure nitrogen compounds was 1.2506 g., as compared to 1.2572 g. for atmospheric nitrogen. This discrepancy led to a careful investigation of atmospheric nitrogen by Rayleigh and Ramsey and to the discovery of argon. Ramsey shortly after identified the gas given off by uranium minerals as the unknown element, helium, whose existence Lockyer had postulated in 1868 to account for a prominent yellow line in the solar spectrum. Subsequent investigation by fractional distillation of the crude argon obtained from air led to the discovery of neon, krypton and xenon, the percentage of the various gases in air being:

He	Ne	A	Kr	Xe
0.0004	0.0012	0.94	0.00005	0.000006 per cent

The natural gas fields of Texas and Kansas contain helium in small amounts, a number of these wells, high in nitrogen content, analyzing between 1 and 2 per cent of the gas.

Research on the radioactive elements (Chap. **XXI**) has shown that the so-called alpha-ray, or particle, is doubly charged helium, and that helium is thus one of the products of the decomposition of these unstable elements. It has been calculated that a gram of radium produces 0.11 cc. of helium per year, and a gram of uranium oxide, U_3O_8, 9.1×10^{-8} cc. The loss of an alpha particle by radium or its isotopes results in the formation of the lowest member of the inert gas group, radon, also called niton. Radon, however, is very unstable, the average life of an atom being only a few days (Chap. **XXI**).

TABLE I

ATOMIC AND PHYSICAL PROPERTIES

	He	Ne	A	Kr	Xe	Rn
Atomic number	2	10	18	36	54	86
Atomic weight	4.00	20.2	39.91	82.9	130.2	222
Isotopes	None	20, 22	36, 40	84, 86, 82	129, 132, 131	222
				83, 80, 78	134, 136, 128	220
					130, 126, 124	
Electrons in various quantum levels,						
1st	2	2	2	2	2	2
2d		8	8	8	8	8
3d			8	18	18	18
4th				8	18	32
5th					8	18
6th						8
Melting point, ° C.	− 268.9 (140 atm.)	− 248.7 (1 atm.)	−189.2	− 169	− 140	− 71
° A	4.2	24.4	83.9	104	133	202
Boiling point, ° C.	− 268.9	− 245.9	−185.7	− 151.8	− 109.1	− 61.8
° A.	4.2	27.2	87.4	121.3	164.0	111.3
Heat of vaporization, cal. per mole, at B.P.	25	405	1,500	2,240	3,200	3,600
Critical temperature, ° C.	− 268	− 220	−117	− 63	15	
Density of liquid	0.126	1.20	1.40	2.6	3.06	4.4
Potential required to ionize gas atoms, volts,						
1st electron	24.5	21.48	15.2	12.7	11	
2d electron	54.1					

2. Physical Properties.—The more important physical properties have been summarized in Table I. The gases are all monatomic, and the low values of the boiling points indicate that their atoms have very little attraction for each other. Indeed, the helium atom is so inert that this element possesses the lowest boiling point of any substance, and by boiling under reduced pressure (below 0.01 mm.), a temperature of 0.7° absolute has been obtained. Considerable pressure (140 atm. at 4.2°) is required to cause liquid helium to solidify and the force of attraction is so small that the heat of solidification at the lowest temperatures is practically zero. Like hydrogen, helium gas heats slightly when expanded at ordinary temperature and the gas must be cooled to the temperature of solid hydrogen (about 11° A.) before it can be cooled by expansion.

The gases are somewhat soluble in water and the solubility increases markedly with increasing atomic weight. Helium and neon are not appreciably absorbed by charcoal cooled in liquid air, but the heavier gases are readily absorbed.

The potentials required to remove electrons from the gaseous atoms are relatively high (Table I) but ionization is, of course, produced when the gas is subjected to an electrical discharge, i.e. bombarded with high speed electrons. The gas under the influence of such a discharge is luminous, due to the light emitted upon the recombination of the electron with the atom, and the characteristic spectrum of each of the elements, thus produced, serves as a ready means of identification.

The weight of an atom is given very closely by the number of protons, or atoms of positive electricity, in the nucleus. It will be seen, that with the exception of helium, the inert gas elements each consist of a number of kinds of atoms, or isotopes, having nuclei of different weights, but having the same net charge on the nucleus, i. e. the same atomic number. The atomic weights, chemically determined, therefore, represent averages and are not whole numbers.

3. Electron Structure and Chemical Properties.—The configuration of the electrons in the various atoms of the group is important, not only as explaining their inertness, but also in connection with the interpretation of the formation of the great majority of chemical compounds. Each inert gas marks the completion of an outer shell of eight electrons, except in the case of helium

which completes the first quantum group containing but two electrons (Table I). These completed groups are so stable that not only are the ionization potentials of the inert gases very high, but the elements preceding and following each inert gas readily gain or lose sufficient electrons to form ions with the same electronic structure, i.e. the completed octet. This is illustrated by the following ions all with the electron structure of neon:

	O^-	F^-	Ne	Na^+	Mg^{++}
Nucleus	+8	+9	+10	+11	+12
Electrons in 1st group	2	2	2	2	2
2d group	8	8	8	8	8

Thus the formation of many binary compounds consists in the transfer of electrons from a metallic element to a non-metallic element with the formation of positive and negative ions of the inert gas type, e.g. in the ions shown above: $Na + F = (Na^+)(F^-)$, and crystals of such compounds are lattices built up of these ions (cf. Append. V for many lattice types). However, it is not to be inferred that all positive ions are of the inert gas type, as most of the noble metals form ions of somewhat different structure (cf. **VII—1**).

Although the statement is generally made that the inert gases form no compounds, a few relatively unstable compounds do exist. Thus helium and hydrogen gases subjected to an electrical discharge contain small amounts of the ions, HeH^+ and HeH_2^+, and the large solubility of the heavier members of the group indicates the formation of unstable hydrates. It is claimed that under a pressure of 15 atmospheres at 0°, krypton forms the hydrate, $Kr \cdot 5H_2O$.

4. Commercial Preparation and Uses.—The United States government operates a plant in Texas for the extraction of helium from natural gas. The process is one of fractional liquefaction. The gas is used in dirigibles and balloons as it has a lifting power only about 10 per cent less than hydrogen and is, of course, non-combustible.

It seems probable that helium will assume considerable importance in deep diving and in deep caisson operations, where

men engaged are subject to "caisson disease." This is due to the solution of nitrogen in the blood at high pressure, and its subsequent escape when the pressure is lowered, forming bubbles in the capillaries, or in the brain or spinal cord. It has been shown that the time required in coming out from under high pressure is greatly reduced by the substitution of a mixture of oxygen and helium for compressed air, on account of the small solubility of helium.

The very low boiling point of helium makes it of special importance in the investigation of the behavior of substances in the neighborhood of absolute zero. Among the more significant changes at these temperatures is the disappearance of the specific heat and coefficient of expansion of solids, and the electrical resistance of many metals (Append. XIV). Although, in general, the resistance of metals decreases with decreasing temperature, there is often an abrupt drop a few degrees above absolute zero: thus, at 6° A., the resistance of lead suddenly decreases a million-fold.

The neon tubes used in electric signs contain the gas under low pressure. The commercial source of the element is the fractionation of atmospheric argon.

Argon is now used extensively in filling electric light globes. The presence of the inert gas decreases the rate of evaporation of the filament, retards the blackening of the bulb, and makes possible the operation of the lamp at a higher temperature, thus greatly increasing its efficiency.

CHAPTER III

OXYGEN

1. The elements of Group VI,—oxygen, O, sulfur, S, selenium, Se, and telurium, Te, are characterized by the presence of six outer or valence electrons, and the tendency to complete the octet of the noble gas structure by the addition of two electrons. Consequently these elements readily form compounds in which they have a valence number of -2. This tendency is the greatest with the smallest atom; hence oxygen is the strongest oxidizing agent and tellurium the weakest. On the other hand the six valence electrons of the neutral atom may be removed, wholly or in part, giving positive valences up to six. In the case of oxygen this can only be done by high potentials in the gas at low pressure, as no other element is capable of removing electrons from oxygen; hence no ordinary compounds exist in which the oxygen must be considered as having a positive valence. This separates it considerably in chemical behavior from the other members of the group, and suggests its separate consideration.

2. Occurrence.—Approximately half by weight of the material of the earth's crust is oxygen, and since the atomic weight of oxygen is less than the average atomic weights of the other elements, it follows that more than half of all the atoms of the earth's crust are oxygen. The most abundant of its compounds are those with silicon and aluminum. The element occurs in the free state in the atmosphere, which is one fifth oxygen by volume. Eight ninths by weight of water and between 40 and 50 per cent of all rocks is oxygen. Compounds are known with all the elements except the noble gases and fluorine.

3. Physical Properties.—In common with the other elements of the family, oxygen exists in several molecular forms. In the gaseous state there are two modifications, ordinary oxygen, O_2, and ozone, O_3. These and probably O_4 also can exist as liquids. Solid oxygen exists in at least three modifications. The more important properties of the oxygen atom and the O_2 molecule are given in Table I.

TABLE I

ATOMIC AND PHYSICAL PROPERTIES OF OXYGEN

Atomic number	8	Density g. per cc. 0° C. and 1 At.	0.0014290
Nucleus { electrons (−)	8	Liquid − 183°	1.13
Nucleus { protons (+)	16	Liquid − 210°	1.24
Atomic weight	16.00	Vaporization at 1 At.	
Isotopes	none	Temperature ° A.	90.1
Electrons in various energy levels, 1st	2	Heat, cals.	1629
2d	6	Fusion	
1st ionization potential of atom, volts	13.5	Temperature ° A.	54.4
Heat of dissociation of O_2 molecule, Kg. Cal.	160	Heat, cals.	105
Dielectric constant of liquid.	1.47	Transition $Solid_1 = Solid_2$	
Magnetic moment of liquid O_2 compared to iron as unity	0.001	Temperature ° A.	43.7
Size of $O^=$ in crystals, cm. $\times 10^8$	1.40	Heat, cals.	177
		Transition $Solid_2 = Solid_3$	
		Temperature ° A.	23.7
		Heat, cals.	17.5
		Solubility per 100 g. water	
		0° C.	0.007
		25° C.	0.004
		100° C.	0.001

The oxygen molecule O_2 is highly magnetic, and since this property is associated with atoms having an odd number of electrons, it is assumed that the electron formula for the molecule is $:\ddot{O}:\ddot{O}:$ rather than $:\ddot{O}::\ddot{O}:$ or $:\ddot{O}:\ddot{O}:$. The variation with concentration of certain of the properties of liquid oxygen dissolved in liquid nitrogen may be explained on the assumption of an equilibrium, $2O_2 = O_4$. The change of this equilibrium with temperature may explain the very large coefficient of expansion of the liquid. In harmony with the assumed structure of O_2 the most likely structure of O_4 would be

$$\begin{matrix} :\ddot{O}:\ddot{O}: \\ :\ddot{O}:\ddot{O}: \end{matrix}$$

4. Chemical Properties.—Oxygen combines directly with all other elements except the halogens, the noble gases, and a few of the most noble metals, and in many of these reactions sufficient energy is evolved to heat the products to the point of incandescence, as in the familiar burning of carbon in air. Very often reactions of oxygen which are rapid at high temperatures will not proceed at low temperatures; thus carbon must be heated before it ignites in air, but many oxidations do go slowly in the cold, e.g. the rusting of iron.

A compound of oxygen with another element is called an oxide, and the valence number of -2 (except in peroxides, Par. 11) is assigned to the oxygen indicating that it has gained two electrons, e.g.

$$2Ca : + : \ddot{O} : \ddot{O} : = 2Ca : \ddot{O} :$$

5. The slowness of many oxygen reactions is doubtless connected with the large energy required to dissociate the oxygen molecule into atoms. Indeed the probable mechanism of most reactions of oxygen is first the addition of two electrons to the O_2 to form a peroxide, where the bond between the oxygen atoms remains unbroken, as illustrated by:

$$Ba : + \begin{matrix} \cdot \ddot{O} : \\ \cdot \ddot{O} : \end{matrix} = Ba \begin{matrix} : \ddot{O} : \\ : \ddot{O} : \end{matrix}$$

The process of oxidation may be examined in detail by arbitrarily dividing the formation of an oxide into the following steps. (This does not imply that the process of oxidation ordinarily occurs in this way.) Using copper oxide by way of illustration:

$$\begin{array}{l} O_2(gas) \xrightarrow{a} O(gas) \xrightarrow{b} O^{--}(gas) \searrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \xrightarrow{f} CuO(solid) \\ Cu(solid) \xrightarrow{c} Cu(liquid) \xrightarrow{d} Cu(gas) \xrightarrow{e} Cu^{++}(gas) \nearrow \end{array}$$

The dissociation of the oxygen molecule, step *a*, involves the absorption of a large amount of energy, as do also steps *c* and *d*, which represents the detachment of copper atoms from the solid mass. The removal of electrons from the metal, step *e*, requires the absorption of still more energy (i.e. the ionization potential). The addition of these electrons to the oxygen atom, step *b*, probably evolves energy; we do not yet know how much, although it is probably not large, since the electrons have to attach themselves to an atom already neutral. It is step *f* which is chiefly responsible for making the net result of the whole process an evolution of energy, and this step must be very large in order to overcome the energy absorption of steps *a*, *c*, *d*, and *e*. Now it is very illuminating to note that step *f* depends for positive ions of the same valence chiefly upon the size of the ions,

being greater the smaller the positive ion. Furthermore, the great stability of oxides, as compared with many other binary compounds, depends upon the fact that the oxygen ion is one of the smallest negative ions. The effect of step *f*, for example, makes the heat of formation of lithium oxide, 142 kg. cals., greater than that of sod um oxide, 101 kg. cals., in spite of the fact that more energy is absorbed in removing the electron from lithium than from sodium.

The above scheme throws light upon differences in the heat of combustion of other substances. Thus a metal of high melting and boiling point, such as platinum, owes its noble character in part to high values for steps *c* and *d*, and not entirely to a high value for step *e*. Again, the high stability of silicon dioxide is related to the large energy evolution of step *f*, which may be inferred from its high melting point and great hardness.

6. Preparation and Uses.—Commercial oxygen is now prepared on a large scale by the fractional distillation of liquid air. The principle of the method may be understood by considering the liquid vapor diagram, Figure 1, for solutions of oxygen and nitrogen. Nitrogen boils at − 195° C. and oxygen at − 183° C. At intermediate temperatures, a solution of the two liquids in equilibrium with the vapors has the composition *b* and the vapor, the composition *a*. Since the gas phase is much richer in nitrogen than the liquid, evaporation results in the liquid becoming richer in oxygen. Simply boiling off the nitrogen from liquid air would not give an efficient separation of the two gases, so the process is carried out in a fractionating column. The cold liquid enters the top of the column; as the liquid evaporates the temperature rises and the liquid increases in oxygen content; the vaporized gas passes up through the colder liquid and loses oxygen, becoming almost pure nitrogen. Oxygen cannot be liquefied above its critical temperature, − 118° C., by any pressure, however great; but the fact that compressed air at

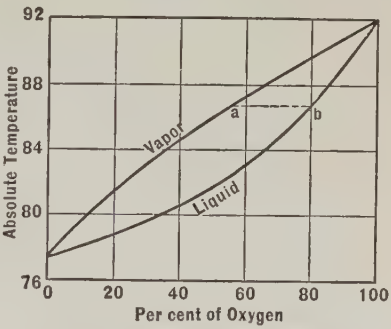


Fig. 1.—Temperature-composition diagram for liquid oxygen and nitrogen.

room temperature cools upon expanding, due to the work done in overcoming the attraction between the molecules (Joule-Thomson effect), makes possible the Linde liquefaction process. Air is compressed to about 3,000 lbs. per sq. in. and allowed to expand. The cool expanded air is led back over the incoming highly compressed air and cools it until finally the temperature drops sufficiently below the critical temperature to permit liquefaction. In the Claude process the compressed air is subjected to an additional cooling effect by doing external work. Some commercial oxygen is prepared by the electrolysis of water; however, unless the electrical energy is very cheap and there exists a ready market for the hydrogen produced at the same time, the electrolytic process cannot compete with the liquid air process.

Barium peroxide was formerly an important source of oxygen, since the reaction, $BaO + \frac{1}{2}O_2 = BaO_2$, is easily reversible. The process was usually carried out at 700° C.; the barium peroxide being first formed from air at a pressure of about 3 atmospheres, and the oxygen then pumped off by reducing the pressure.

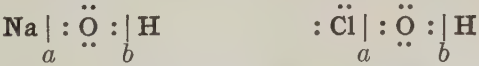
Sodium peroxide (cf. **IV—11**) is a convenient source of oxygen in small quantities. A common laboratory method for the preparation of oxygen consists of the decomposition of potassium chlorate using manganese dioxide as a catalyst at about 200° C.: $2KClO_3 = 2KCl + 3O_2$. In the absence of a catalyst, oxygen is evolved but slowly; most of the chlorate being converted into perchlorate, which is much more stable. In the early investigations of oxygen by Scheele, Priestley, and Lavoisier (about 1775) much use was made of the compounds HgO, MnO_2, PbO_2, and KNO_3, all of which give oxygen upon heating.

The present commercial importance of oxygen has resulted from the development of the oxy-acetylene torch in welding and cutting metals. Oxygen for this purpose is sold in heavy cylinders under a pressure of about 2,000 lbs. per sq. inch. The oxy-hydrogen torch, although not producing as high a temperature as the oxy-acetylene flame, is also of wide industrial use. Pure oxygen is used in the treatment of pneumonia and in cases of asphyxiation; and mixtures of oxygen with nitrous oxide or ether are administered in producing anesthesia. It is also used to maintain the oxygen content of the air in submarines.

The "hardening" of certain oils is accelerated by using pure oxygen. Charcoal, cotton, or other cellulose soaked in liquid oxygen form high explosives known as "oxylignite."

7. Oxides, Bases, Acids.—The various types of oxides with different elements correspond to all the possible valences of the positive elements from + 1, as in Cu_2O, to + 8, as in OsO_4. In addition, a number of mixed oxides occur with elements forming oxides of more than one valence, for example Pb_3O_4, which is $(PbO)_2PbO_2$, and Fe_3O_4, which is $FeO \cdot Fe_2O_3$. In the crystalline state, if the force of attraction between the positive kernel and the oxide ion is not too great, the oxides crystallize in the completely polar type of structure: for example, the CaO crystal is a lattice of Ca^{++} and O^{--} similar to the sodium chloride structure, and there are no molecules of CaO. On the other hand, large attractive forces allow the molecule to preserve its identity in the solid as in carbon dioxide.

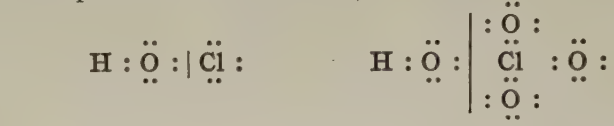
Oxides of metals of low valence react with water to form bases, e.g. $Na_2O + H_2O = 2NaOH$, $MgO + H_2O = Mg(OH)_2$; while oxides of non-metals, and even of metals of high valence react with water to form acids: e.g. $Cl_2O + H_2O = 2HOCl$; $SO_2 + H_2O = H_2SO_3$; $CrO_3 + H_2O = H_2CrO_4$; $Sb_2O_5 + 3H_2O = 2H_3SbO_4$. In all of these compounds an atom of oxygen separates a hydrogen atom from the remainder of the molecule; and the basic or acidic character seems to depend largely upon the relative attractive forces between the oxide ion and the hydrogen ion, on the one hand, and the remainder of the molecule on the other, modified by the energy of hydration of the resulting ions. Thus NaOH is a base because the cleavage occurs more easily at *a*, Figure 2; while HOCl is an acid because it occurs at *b*. (Cf. Hildebrand, *Princ. of Chem.*, p. 266.)



This may be connected with the disparity in size between Na^+, H^+ and Cl^+. If these ions in the compounds are assumed, as an approximation, to be simple spheres of charge, e, and radius, r, the energy of attraction would be $ee'/(r + r')$. Since Na^+ is so much larger than Cl^+, the distance $r + r'$ would be much larger, $2.35 \cdot 10^{-8}$ cm. vs. $1.66 \cdot 10^{-8}$ cm., and the energy of separation from O^{--} much smaller. That the separation occurs

at *b* rather than at *a* for ClOH, in spite of the small size of the H^+, may be attributed to the large energy of hydration of the hydrogen ion (cf. I—7) which modifies the above considerations.

The larger charge on an atom of high valence also accounts for its greater tendency to give acidic properties. For example, if we compare HClO with $HClO_4$,



and consider that in the latter the electrons largely belong to the oxygen, making the chlorine + 7, while in the former the chlorine has lost but 1 electron, making it + 1, we may expect the energy of separation of OH^- to be roughly seven times as great in the latter. It is, therefore, correspondingly easier for H^+ to be detached from the latter.

TABLE II

VALUES FOR $\frac{e'e}{r+r'}$ FOR OXIDE ION ($r = 1.40 \cdot 10^{-8}$ CM.) AND CERTAIN POSITIVE IONS

	Li^+	Be^{+2}	B^{+3}	C^{+4}	N^{+5}		
Radius cm. $\times 10^8$	0.60	0.31	0.20	0.15	0.11		
$\frac{ee'}{r+r'}$	1.0	2.32	3.74	5.16	6.62		
Hydroxide	LiOH strong base	$Be(OH)_2$ ampho-teric	$B(OH)_3$ ampho-teric	$CO_2(OH)_2$ weak acid	NO_2OH strong acid		
	Na^+	Mg^{+2}	Al^{+3}	Si^{+4}	P^{+5}	S^{+6}	Cl^{+7}
Radius cm. $\times 10^8$	0.95	0.65	0.50	0.41	0.34	0.29	0.26
$\frac{ee'}{r+r'}$	0.86	1.96	3.16	4.42	5.76	7.10	8.44
Hydroxide	NaOH strong base	$Mg(OH)_2$ weak base	$Al(OH)_3$ ampho-teric	$SiO_2(OH)_2$ weak acid	PO_2OH strong acid	$SO_2(OH)_2$ strong acid	ClO_3OH strong acid

Table II illustrates the change from basic to acidic character dependent upon the sizes of the atoms and their charges. We see that similar energy values yield similar characteristics.

8. Analytical Properties.—Both oxygen and nitrous oxide will cause a glowing splinter to burst into flame, but oxygen may be

distinguished from the latter by the production of dark brown fumes with nitric oxide. The gas is usually determined quantitatively in a mixture of gases by determining the decrease in volume upon contact with various liquids or solids which absorb oxygen, such as, (1) a solution of cuprous chloride in hydrochloric acid, (2) alkaline solution of pyrogallol, (3) phosphorus. A very delicate test for small quantities of oxygen is the deep red color produced by the action of oxygen upon an alkaline solution containing ferrous iron and pyrocatechol.

9. Water.—Water plays such an important role in chemistry that its physical constants are of especial significance. For a substance of low molecular weight, its **melting point**, 0° C., and **boiling point**, 100° C., are extremely high, indicating high attractive forces between the molecules. The high **dielectric** constant, 81 at 18° C., shows that the molecules are highly polar, which would account for the large intermolecular attraction, for 2 dipoles would attract each other. The unusual solvent action of water for salts is also to be correlated with its high dielectric constant, since the force of attraction between ions varies inversely as the dielectric constant of the medium. Water is unusual in possessing a point, 4° C., of maximum **density** (Append. VIII). This may be connected with the fact that water is one of the few substances whose liquid form ($d = 1.00$ at 4° C.) is denser than the solid ($d = 0.917$). In ice the molecules are combined in a way that involves a looser packing than in the liquid, and as the temperature of the liquid approaches 0°, there are doubtless formed an increasing proportion of these same molecules in the liquid. This change counteracts the increase in density uniformly found when only one molecular species is present. Complete **vapor pressure** tables for water and ice are given in Append. X. The simple phase diagram for "solid, liquid, vapor" is represented in Figure 2.

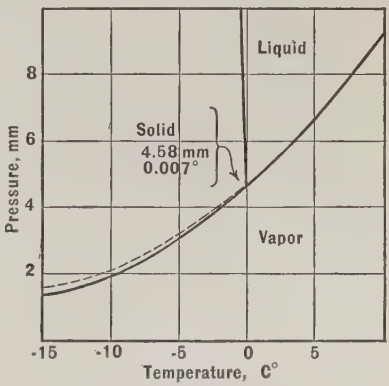


FIG. 2.—Temperature-pressure for ice, water, and vapor.

Since the density of the solid is less than that of the liquid, the melting point is decreased by pressure. At high pressures ice exists in a number of allotropic modifications, and as several of these are denser than the liquid, they may be obtained under high pressure at temperatures above 0°, as shown in Figure 3.

Crystal structure data seem to indicate that in the ordinary form of ice each oxygen atom is surrounded by four other oxygen atoms with a hydrogen atom located on the line joining the oxygens.

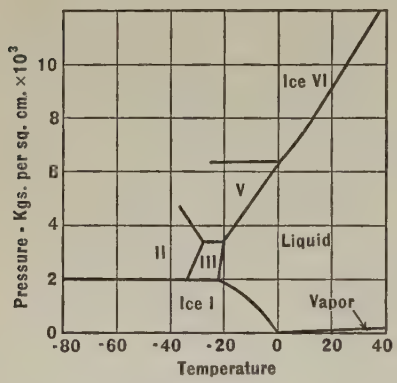


Fig. 3.—Modification of ice at high pressures.

The **heat of fusion** is 80 cal. per gram and the **heat of vaporization**, 540 cal. per gram. The **lowering of the freezing point** and the **elevation of boiling point** per mole of solute in 1,000 g. of water are 1.86° and 0.52° respectively. The lowering of the freezing point of water by common salt is important in refrigeration. The freezing point diagram is given in Figure 3, Chapter IV. One of the lowest eutectics given with water is that of $CaCl_2 \cdot 6H_2O$. A mixture of 7 parts of snow and 10 parts of $CaCl_2 \cdot 6H_2O$ gives a temperature of − 55° C. (cf. Figure 2, Chapter V).

The **surface tension** of water at 20° is 72.5 dynes per cm. The **compressibility** at 20° is 43×10^{-6} cc. per megabar. The **specific heat** of 1 g. of water at 15° is taken as unity in the definition of the calorie. The variation of its specific heat with temperature is as follows: 0°, 1.0088; 30°, 0.9988; 50°, 0.9996; 100°, 1.0099. The **heat of formation** per mole of H_2O at 25° is − 68,270 cal. The

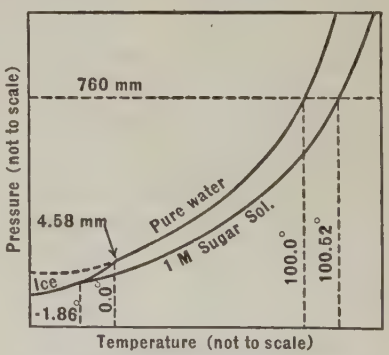


Fig. 4.—Diagrammatic representation of the effect of a solute upon the vapor pressure, boiling point and melting point of water.

heat of ionization, $H_2O = H^+ + OH^-$, $-13{,}200$ cal. is of course the negative of the heat of neutralization of dilute solutions of strong acids and bases. The **decomposition voltage** of water upon electrolysis is 1.23 volts plus an overvoltage depending upon the nature of the electrodes due to the slowness of the electrode reactions. The **specific conductivity** of the purest water at 20° C. is about 1×10^{-7} reciprocal ohms.

10. Water is easily purified from non-volatile substances by distillation; however, to prepare water free from volatile acids, bases, and organic material, elaborate precautions must be taken. This is usually done by first distilling from an alkaline solution of permanganate to remove organic material and volatile acids, especially carbonic, and then redistilling from non-volatile acid solution to remove volatile alkalies, especially ammonium. If the vapor is condensed in air it will contain dissolved gases, hence the distillation is carried out in vacuum. Due to the solubility of glass in water, the condenser is made of quartz, tin, or silver. The so-called "softening of hard water" is discussed under calcium (cf. V—11).

11. Hydrogen Peroxide.—The formation of peroxides as intermediate products in the direct oxidation by oxygen has been mentioned (Par. 4). These compounds may be considered as derivatives of hydrogen peroxide, H_2O_2. The valence number of the oxygen is -1. In terms of molecular structure peroxides consist of oxygen linked to oxygen to form the group $:\ddot{O}:\ddot{O}:$.

The oxidation of certain metals by moist oxygen results in the formation of the oxide and hydrogen peroxide: e.g. $Zn + O_2 + H_2O = ZnO + H_2O_2$. The mechanism of this reaction may be the formation of zinc peroxide and its subsequent hydrolysis. Hydrogen peroxide is also formed by the action of ultraviolet light upon water: $2H_2O = H_2O_2 + H_2$. High anodic potentials are capable of oxidizing the oxygen in many of its compounds to the peroxide valence: for example, concentrated sulfuric acid is oxidized to peroxydisulfuric acid $\mathrm{HO{-}\overset{O}{\overset{\|}{S}}{-}O{-}O{-}\overset{O}{\overset{\|}{S}}{-}OH}$. This acid may then be hydrolysed to form hydrogen peroxide and sulfuric acid. Some commercial hydrogen peroxide is prepared in this manner, but the greater portion is prepared by the action of cold sulfuric acid upon hydrated barium peroxide: $BaO_2 + H_2SO_4 = BaSO_4$

$+ H_2O_2$. The peroxide being less volatile than water may be concentrated by evaporation under reduced pressure.

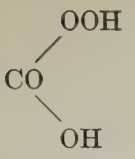
12. Pure hydrogen peroxide is a faint blue syrupy liquid melting at $-2°$. It has a vapor pressure of 47 mm. at 80° C. Violent decomposition occurs if heated much above this temperature. The dielectric constant of the liquid is given as 93, a value even higher than that of water. The water solutions are fairly stable if kept in a cool, dark place. Acetanilid is usually added to the commercial product to act as a preservative. The decomposition into water and oxygen, $H_2O_2 = H_2O + \frac{1}{2}O_2$, is catalyzed by many substances, for example, silver, manganese dioxide, hydrogen bromide, sodium hydroxide, saliva, and blood. The ordinary commercial preparation, a 3 per cent solution, is often called a 10 "volume solution" from the fact that it will evolve about 10 times its volume of oxygen.

Peroxide is a powerful oxidizing agent in both acid and alkaline solutions (Par. **14**), the oxygen being reduced from a valence number of -1 to -2. One of the most important reactions of hydrogen peroxide is the quantitative oxidation of iodide: $2I^- + H_2O_2 + 2H^+ = I_2 + 2H_2O$. It also acts as a reducing agent, the oxygen being oxidized from a valence number of -1 to 0, but a fairly powerful oxidizing agent is required to bring about its oxidation in acid solution. As examples we have the quantitative reduction of permanganate: $5H_2O_2 + 2MnO_4^- + 6H^+ = 2Mn^{++} + 5O_2 + 8H_2O$, and the reduction of silver oxide: $Ag_2O + H_2O_2 = 2Ag + O_2 + H_2O$.

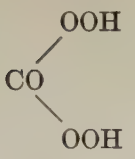
Hydrogen peroxide is used as an antiseptic and as a bleaching agent for hair, silk, feathers, ivory, etc.

Delicate qualitative tests for peroxide are the reactions with chromate or titanic sulfate in acid, forming highly colored peroxy-acids. The peroxychromic acid is a bright blue compound, soluble in ether, and the peroxytitanic acid is yellow.

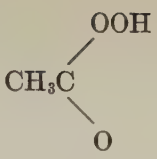
13. Peroxy-acids.—There are a large number of acids containing peroxy-oxygen. These may be considered as derivatives of oxy-acids formed by the substitution of $-OOH$ in place of OH^-, for example



monoperoxycarbonic



diperoxycarbonic



peroxyacetic

The elements forming peroxy-acids are B, C, Ti, Ge, Sn, N, P, V, Cb, Ta, S, Cr, Se, Mo, N, and U. Many of these acids are discussed under the respective elements. The most important is probably peroxydisulfuric acid, $H_2S_2O_8$.

14. Ozone.—The density of ozone corresponds to the molecular formula O_3. The reaction, $3O_2 = 2O_3$, absorbs 35.0 kg. cal., and the formation of ozone from oxygen is therefore favored by high temperature. The equilibrium mixture of the gas at 3,000° C. probably contains about one per cent of ozone. Sufficient energy to bring about the transformation may be supplied either by ultraviolet radiation or by a silent electrical discharge. Ultraviolet radiation of about 260 $\mu\mu$ (corresponding to 4.7 volts) is absorbed by oxygen molecules. These highly activated molecules then react to form ozone. The outer portion of the earth's atmosphere must contain large concentrations of ozone formed in this manner by the sun's radiation; indeed the blue color of the sky is attributed to its presence. The silent electrical discharge is the principal commercial means of forming ozone. This involves the action of electrons shot off from high-potential surfaces upon oxygen molecules. Ozone is also formed under powerful oxidizing conditions, as in the action of fluorine upon water, and by the oxidation of water by a high anodic potential, as, for example, in the electrolysis of aqueous sulfuric acid using a very high current density

Reference to the table of oxidation reduction potentials shows that ozone is itself a very powerful oxidizing agent, second only to fluorine. The gas is fairly stable toward decomposition into oxygen, and condenses to a blue liquid at about − 115°. It has a very pungent, characteristic odor, and unlike oxygen it is not magnetic. Ozone is more soluble in water than is oxygen, and is still more soluble in alkaline solution. The latter solution is claimed to contain $O_4^=$, the ion of "ozonic acid." By the analogy of ozone and sulfur dioxide this acid corresponds to

sulphurous acid, and although the free acid is not known, potassium tetroxide, K_2O_4, may be considered to be one of its salts.

Ozone is used in sterilization of water; bleaching of paper pulp, fabrics, and flour; the resinification of oils; and as a deodorant for air in crowded interiors. (Its bactericidal properties in this connection seem not to be very great.) Qualitatively it may be detected by its peculiar odor, by its action upon potassium iodide, and by the blackening of silver.

15. Oxidation-reduction Potentials.—Important oxidation reduction potentials involving oxygen and its oxides have been summarized in Table III. Since the first step in the reduction of oxygen is generally the formation of the peroxide, this potential, equation (2) is an important factor in determining the action of oxygen. However the reverse reaction, that is the oxidation of water, does not involve the formation of peroxide as an intermediate step and depends upon equation (5).

TABLE III

OXIDATION-REDUCTION POTENTIALS

	$Volts_{25°}$
(1) $2OH^- = \frac{1}{2}O_2 + H_2O + 2E^-$	− 0.398
(2) $H_2O_2 = O_2 + 2H^+ + 2E^-$	− 0.68
(3) $3OH^- = HO_2^- + H_2O + 2E^-$	− 0.87
(4) $H_2O = \frac{1}{2}O_2 + 2H^+ + 2E^-$	− 1.23
(5) $2H_2O = H_2O_2 + 2H^+ + 2E^-$	− 1.78
(6) $O_2 + H_2O = O_3 + 2H^+ + 2E^-$	− 1.9

CHAPTER IV

GROUP I. ALKALI METALS

1. The first group of the periodic system contains the elements lithium, sodium, potassium, rubidium, and cesium. They are called the alkali metals because their hydroxides are all soluble bases or alkalies. The most important common characteristics of these elements are the single electron in the outermost energy level of their atoms, and the comparatively low voltage required to detach this electron from the atom, as shown by the ionizing potentials given in Table I.

Although the outer electron is easily removed, the underlying ones can be removed only by very high potentials; hence ordinary chemical reactions involve the loss or transfer of only a single electron per atom, as illustrated by the equation: $M = M^+ + E^-$. Accordingly these elements display invariably a valence of $+1$ in their compounds.

2. Atomic and Physical Properties.—Many of the physical and chemical properties of these elements may be correlated with the structures of their atoms. (Cf. Table I, also *Prin. of Chem.*, Chap. XVII.) Thus in the solid state the electrons are held so loosely that they can readily pass from association with one atom to another under the impulse of an electric potential; hence these elements show in a high degree the conductivity and other properties characteristic of metals. Moreover, since there are not enough outer electrons to serve to bind an atom firmly to all of its neighbors in the solid state, we find these metals to be soft, and easily fusible.

Another phenomenon connected with the easy loss of electrons by these metals is their solubility in liquid ammonia to give highly conducting solutions. The process of solution is accompanied by an ionization of the metal atom whose electron attaches itself to a molecule of ammonia; thus, M (solid) = M^+ (in NH_3) + E^- (ammoniated). The alkali metals all give solutions in ammonia of the same blue color, which is due to the solvated electron, the metal ion being colorless in all cases. The addition of MCl increases the concentration of M^+ and diminishes the

blue color in accordance with the mass law. The alkaline earth metals are soluble in liquid ammonia in this way to a smaller extent, and the nobler metals, which hold their electrons more firmly, do not dissolve at all in liquid ammonia.

The metal vapors are some what associated into diatomic molecules at the boiling points of the liquids. The heats of dissociation of the Na_2 and K_2 molecules are 22,500 and 15,000 cal. respectively

The nuclei of potassium and rubidium are not altogether stable, as shown by their slight radio-activity (cf. **XXII—16**).

TABLE I

Atomic and Physical Properties

Element	Lithium	Sodium	Potassium	Rubidium	Cesium
Latin Name	Lithium	Natrium	Kalium	Rubidium	Cesium
Symbol	Li	Na	K	Rb	Cs
Atomic weight	6.94	23.00	39.10	85.44	132.81
Atomic number	3	11	19	37	55
Melting point ° C.	186	97.5	62.3	38.5	26
Boiling point ° C.	1,200	880	760	700	670
Density 20° C.	0.53	0.97	0.86	1.53	1.90
Isotopes	6, 7	none	39, 41	85, 87	none
Nucleus { Electrons (−)	3 4	12	20 22	48 50	78
Nucleus { Protons (+)	6 7	23	39 41	85 87	133
Electrons in various quantum levels, 1st	2	2	2	2	2
2d	1	8	8	8	8
3d	—	1	8	18	18
4th	—	—	1	8	18
5th	—	—	—	1	8
6th	—	—	—	—	1
Ionizing potentials of gaseous atoms, volts	5.37	5.12	4.32	4.16	3.88
Potential required to remove electrons from solid metal	2.35	2.12	—	—	—
Potential between metal and normal aqueous soln. of ion; $M = M^+_{aq} + E^-$	2.96	2.71	2.92	2.92	—
Heat of hydration of gaseous ions, kg. cals.	119	96	77	72	70
Atomic radius in crystals, cm $\times 10^8$ (if $Cl^- = 1.81$)	0.60	0.95	1.33	1.48	1.69

3. Spectra.—Spectra of the alkali metals are easily excited; even the comparatively low temperature of a Bunsen flame

suffices to disturb the outer, valence electron; moreover, since the single valence electron alone is disturbed, unless a high voltage spark is used, their spectra are comparatively simple. The wave length (in mm. $\times 10^{-6}$) of the prominent lines in the flame spectra are as follows: lithium, 670 red, 620 orange, fainter; sodium, 590 yellow; potassium, 768 red, 404 violet; rubidium, 780 red, 420 blue, 358 violet; cesium, 457 blue, 388 violet.

4. Chemical Properties.—Since the metals all give up their outer electrons so easily to other substances they are chemically very reactive. Thus, they all decompose water vigorously, the water taking up the electrons and giving hydroxide ion and hydrogen gas: M (solid) + $H_2O = \frac{1}{2}H_2 + M^+ + OH^-$. With potassium, rubidium, and cesium the amount of heat developed is so great that the metal takes fire almost instantly when thrown upon water.

5. The ease with which an electron is removed from the metal increases regularly in going from lithium to cesium, as shown by the ionizing potentials; hence we would expect that the ease with which the metal forms any one of its compounds would increase from lithium to cesium; and, conversely, the difficulty of reducing the metal from its compounds would be greatest for cesium and least for lithium. This is in general the case, although the simple prediction is somewhat modified by the different sizes and attractions of the resulting ions. The ionizing potentials refer to the reaction: M (gas) = M^+ (gas) + E^- (gas), while the reaction between solid metal and water, previously given, involves in addition the hydration of the M^+. This sets free a large amount of energy, and just as the smallest ion, lithium, attracts an electron most strongly, so also it attracts water molecules most strongly, a fact which helps lithium metal to react with water to give it a high electrode potential in water solution, as shown in Table I, instead of the lowest as one would conclude from the ionizing potentials alone.

This point may be clarified by the aid of the following scheme representing the formation of MCl by a series of steps, which give out or absorb energy, as the case may be.

$$\begin{array}{ccccccc} & & a & & b & & \\ \mathrm{M\ (solid)} & \rightarrow & \mathrm{M\ (gas)} & \rightarrow & \mathrm{M^+\ (gas)} & & \\ & & + & & + & \searrow^{e} & \\ & & c & & d & & \\ \mathrm{Cl_2\ (gas)} & \rightarrow & \mathrm{Cl\ (gas)} & \rightarrow & \mathrm{Cl^-\ (gas)} & \rightarrow & \mathrm{MCl\ (gas)} \rightarrow^{f} \mathrm{MCl\ (solid)} \\ & & + & & - & & - \end{array}$$

We have marked each step + in which the system would absorb heat, and each − in which the system would lose heat. If potassium were substituted for lithium, steps *c* and *d* would naturally remain the same; step *a* would become smaller (Table I) showing that potassium is more easily fused and vaporized; step *b* would have a smaller positive value (see Ionizing Potentials); but step *e* would also have a smaller negative value, the last two effects thus tending to offset each other. Although the heats evolved in formation per mole follow for most compounds the order expected from the ionizing potentials, and illustrated by the iodides, bromides, and chlorides in Table II, the fluorides show the reverse order on account of the small size of the lithium and fluoride ions, allowing close approach and a large negative value for step *e*.

TABLE II

HEATS EVOLVED IN FORMATION OF ALKALI HALIDES, KILOGRAM CALORIES PER MOLE

	Li	Na	K	Rb	Cs
Iodides	71	76	85	88	90
Bromides	87	90	97	99	101
Chlorides	97	99	105	105	106
Fluorides	145	137	135	133	132

For the same reason, the compounds with other small atoms usually show the greatest stability with lithium rather than with cesium. Other examples include the hydrides, carbides, nitrides, and oxides.

The smaller size and smaller ionizing potential of lithium tends to ally it somewhat with the elements of Group II, particularly magnesium. This is in harmony with the corresponding resemblance between beryllium and aluminum, boron, and silicon. (Cf. III—2 and Hildebrand, *Prin. of Chem.*, p. 269.) This

resemblance is illustrated by the low solubility of its carbonate and phosphate, as well as by the stability of the compounds mentioned in the preceding paragraph.

6. The complete transfer of electrons by the alkali metals in the formation of their compounds is illustrated again by the crystal structure of their halides. (Cf. *Prin. of Chem.*, p. 320.) All except those of cesium crystallize in a cubic lattice of the sodium chloride type (Append. V) in which the sodium and chlorine atoms alternate, and each atom of one kind is surrounded by six atoms of the other, *all equidistant from it.* It is not possible, to designate any sodium atom as belonging to any particular chlorine atom. There are, therefore, no molecules of NaCl present in the crystal. Now if each sodium atom retained its original electron it would be bound by it to a particular chlorine atom; the absence of such binding shown by the symmetry of the crystal lattice is evidence that the electrons have passed over to the chlorine atoms, giving each an extra electron, making it chloride ion, Cl^-, and leaving the sodium atom as sodium ion, Na^+. Indeed, we have only to melt the crystal, releasing these ions from their fixed positions, and the substance becomes an excellent electric conductor, quite unlike a substance such as sulfur, which is an insulator in the liquid as well as the solid form. The solution of an alkali halide in water merely substitutes the attraction of its ions for water for their attraction for each other. The energy of hydration is very high (Table I) and serves to overcome the large electrostatic force responsible for the cohesion of the crystal.

The fact that lithium has the largest energy of hydration is noteworthy in connection with the high solubility of many of its salts. The salts of low solubility are those where there is an especially high attraction between the lithium ion and the negative ion in the crystal, as in the case of the fluoride.

7. Occurrence.—From the average composition of outer portions of the earth it is estimated that there is present 2.36 per cent sodium, 2.28 per cent potassium, and 0.01 per cent lithium. Rubidium and cesium are usually present in all potassium containing rocks, but only in very small amounts. Spectral lines of lithium and sodium are prominent in the sun. The spectra of the other alkalies are not found in the chromosphere of the sun doubtless because the temperature is sufficient to

remove the outer electron completely. Potassium and rubidium can, however, be observed in the cooler portions.

TABLE III

SUMMARY OF THE MORE IMPORTANT REACTIONS OF THE ALKALI METALS

$4M + O_2 = 2M_2O$	Li only
$2M + O_2 = M_2O_2$	Li slightly, Rb and Cs spontaneously in dry air
$2M + 2O_2 = M_2O_4$	K, Rb, Cs
$6M + N_2 = 2M_3N$	Li only
$2M + X_2 = 2MX$	With halogens
$2M + S = M_2S$	With Te also
$3M + P = M_3P$	With As, Sb also
$2M + 2H_2O = 2M^+ + 2OH^- + H_2$	
$2M + 2C_2H_5OH = 2C_2H_5OM + H_2$	
$2M + 2NH_3$ (gas) $= 2NH_2M + H_2$	
$3M + AlCl_3 = 3MCl + Al$	At high temperature
$6M + B_2O_3 = 3M_2O + 2B$	At high temperature
$2M + H_2 = 2MH$	
$5M + MNO_3 = 3M_2O + \frac{1}{2}N_2$	

Sea water contains about 2.8 per cent of sodium chloride and 0.08 per cent of potassium chloride, and the evaporation of inland seas has resulted in enormous deposits of these salts. These deposits of chlorides, and also deposits of carbonates, sulphates, and nitrates are discussed under the corresponding salts. Most plants contain from 4 to 6 times as much combined potassium as sodium, a fact responsible for the use of potassium compounds as one of the important fertilizers. The ashes of sea weeds, however, contain more sodium than potassium carbonate, with certain exceptions. The alkalies are found in varying amounts in nearly all silicates. Several lithium complex aluminum silicates are of importance, such as lepidolite, $Li_3Al(SiO_3)_3$, and petalite, $LiAl(Si_4O_{10})$. Potassium feldspar, $KAlSi_3O_8$, occurs in immense deposits.

8. Preparation and Uses of the Metals.—Lavoisier, in 1793, predicted that the "alkalies" would prove to be metallic oxides. Sir Humphrey Davy isolated sodium and potassium in 1807 by electrolysis of their hydroxides. This method is today the one used in the technical preparation of sodium. The metals may also be prepared by the reduction of the hydroxide or carbonate at moderately high temperatures, with iron, calcium, carbon, or other reducing agents. The reduction by less electropositive elements is accomplished through the greater volatility of the

alkali metals. The reduction with calcium furnishes probably the simplest laboratory method of preparing rubidium and cesium.

Many attempts have been made to prepare sodium by the electrolysis of the fused chloride, but the mechanical difficulties arising from the corrosive action of the molten chloride and hot chlorine have been too great for successful operation. The Castner process, which is now in general use, employs the fused hydroxide at a temperature slightly above its melting point. Both hydrogen and alkali metal are liberated at the cathode. The liquid metal floats to the surface of the molten hydroxide, where it is protected from oxidation by the atmosphere of hydrogen which is maintained, whence it is drawn off from time to time.

The only one of these metals to find any considerable commercial use is sodium. The most important of its uses are the manufacture of sodium peroxide and cyanide, and in the preparation of organic chemicals and dyes where a powerful reducing agent is required.

9. Alloys.—Sodium amalgamates with mercury with almost explosive violence. The amalgam is often used in place of the solid metal as a reducing agent. An alloy of 24 per cent sodium and 76 per cent potassium is liquid down to $-12.6°$. This is sometimes used to remove traces of water from gases. Lithium is more like the elements of the second and third groups (Par. 25) and therefore alloys with them more readily than do sodium or potassium. Its alloy with aluminum may achieve commercial importance on account of its very low density.

10. Hydrides.—Compounds of the type MH are formed by the direct action of hydrogen upon the heated metals. These compounds are salt-like in appearance and are of interest because of their analogy to the alkali halides. The electrolysis of the molten hydride results in the liberation of hydrogen at the anode, indicating that the hydrogen possesses a negative valence. Sodium and potassium hydride react with carbon dioxide, forming sodium formate: $NaH + CO_2 = HCOONa$.

11. Oxides.—The direct action of oxygen upon lithium produces the monoxide, Li_2O, and a trace of lithium peroxide, Li_2O_2; with sodium the dioxide, Na_2O_2, is produced; and with potassium, rubidium, and cesium the oxides, MO_2 and M_2O_4, result. The

monoxides cannot be prepared by dehydration of the hydroxides, but may be formed by the action of the metal upon the nitrate, e.g. $5K + KNO_3 = 3K_2O + \frac{1}{2}N_2$. The higher oxides all contain peroxide oxygen. The dioxides are salts of hydrogen peroxide, and the tetroxides salts of hypothetical ozonic acid, H_2O_4 (cf. **III—12**). The only oxide of commercial importance is Na_2O_2 which is used extensively as a source of oxygen and hydrogen peroxide under the name of "oxone." The peroxide hydrolyzes in water with the formation of H_2O_2. When a small amount of water is used upon an excess of sodium peroxide, the liberated hydrogen peroxide decomposes with evolution of oxygen. Sodium peroxide is made commercially by heating sodium in dry air free from carbon dioxide to a temperature somewhat above 300°. The principle of counter currents is employed.

12. Hydroxides.—The older methods of manufacture used the reaction between a dilute solution of the alkali carbonate and milk of lime. $2Na^+ + CO_3^{--} + Ca^{++} + 2OH^- = CaCO_3 + 2Na^+ + 2OH^-$. Two thirds of the hydroxide consumed in this country is produced by this process. The balance is manufactured by the electrolysis of a solution of the alkali chloride, a process which results in the formation of the hydroxide and hydrogen at the cathode and chlorine at the anode. The cell reaction is: $2H_2O + 2Cl^- = 2OH^- + H_2 + Cl_2$. In carrying out this electrolysis the cell must be constructed so as to prevent the interaction of the hydroxide and the chlorine, which would give hypochlorite at low temperatures or chlorate at higher temperatures. This problem is not altogether easy since the hydroxide moves toward the anode under the electric field and the chlorine is somewhat soluble in the brine. The **Nelson** cell used most extensively in the United States, has a carbon anode and perforated steel cathode. The brine percolates through the cell and out the perforations in the cathode at such a rate that the hydroxide is swept back and prevented from reaching the anode. The liquid coming from the cell contains a mixture of the hydroxide and chloride. Upon evaporation the greater portion of the chloride is precipitated.

The **Castner-Kellner** process takes advantage of the fact that sodium or potassium may be electrolyzed from a concentrated brine solution with a mercury cathode to form a dilute amalgam, and this amalgam will react with water to form a dilute hydroxide

solution. The cell employed is ingeniously constructed for the continuous operation of these reactions. The process gives a very pure product.

Commercial sodium and potassium hydroxides may contain, in addition to large amounts of chloride, some carbonate, sulphate, nitrate, phosphate, acetate, and peroxide, as well as small amounts of the other alkalies. The hydroxide, sold as "pure by alcohol," has been dissolved in alcohol which separates out most of the impurities, but leaves a little chloride, carbonate, and acetate. A hydroxide free from the negative impurities may be made by treating a solution of purified alkali carbonate with silver carbonate and boiling the resulting solution with carefully purified lime in a silver dish.

TABLE IV

PRODUCTION AND CONSUMPTION OF SODIUM COMPOUNDS IN UNITED STATES IN 1927

Production of Sodium Compounds	Tons
Chloride	7,000,000
Carbonate	1,950,000
Hydroxide	550,000
Silicate	450,000
Sulphate	250,000
Bicarbonate	125,000
Borate	50,000
Chromates	30,000
Thiosulphate	25,000
Sulphide	20,000
Sulphite	15,000
Hypochlorite	12,000
Nitrate	3,000
Fluo-silicate	1,500
Fluoride	1,000
Metal	500
Acetate	400
Benzoate	350
Citrate	300

Consumption of Sodium Carbonate	Tons
Glass	650,000
Hydroxide (lime reaction)	500,000
Soap	220,000
Chemicals	200,000
Cleaning compounds	125,000
Paper	80,000
Water softening	70,000
Petroleum	40,000
Textiles	35,000

Consumption of Sodium Hydroxide	Tons
Soap	100,000
Chemicals	85,000
Petroleum	80,000
Rayon	70,000
Lye	45,000
Exports	50,000
Textiles	40,000
Rubber reclaiming	30,000
Pulp and paper	30,000
Vegetable oils	13,000
Storage batteries	5,000

The consumption of sodium hydroxide in the more important

industries is given in Table IV. Potassium hydroxide is used less extensively than the sodium compound because of its greater cost. Its principal use is in the manufacturing of soft soap, which owes its properties to the greater solubility of the potassium compound.

13. Sodium Carbonates and Bicarbonates.—Sodium carbonate is found in high concentration in the lakes of many arid regions. Mono Lake and Owen's Lake in California contain millions of tons capable of rather cheap extraction.

The ashes of certain sea plants were formerly the common source of the salt, but it is now manufactured from sodium chloride. The **Le Blanc process** was the earliest (1791) method employed on a large scale for the conversion of chloride to carbonate. The steps in the process are:

(1) $NaCl + H_2SO_4 = NaHSO_4 + HCl$
(2) $NaHSO_4 + NaCl = Na_2SO_4 + HCl$
(3) $Na_2SO_4 + 2C = Na_2S + 2CO_2$
(4) $Na_2S + CaCO_3 = Na_2CO_3 + CaS$

Reaction (1) occurs readily upon gentle heating, but reaction (2) requires a much higher temperature. The third and fourth steps are carried out in a rotary furnace at a temperature of 700–1,000°, the charge consisting of a mixture of the sodium sulfate with coal dust and lime stone. The product, called "black ash," is extracted with water and impure carbonate, $Na_2CO_3 \cdot H_2O$, obtained by crystallization. The sulfide residue is usually oxidized to free sulfur and thus made a profitable by-product.

The **Solvay** or **ammonia** process has now largely superseded the Le Blanc. It is based upon the reactions:

(1) $Na^+ + Cl^- + NH_3 + H_2O + CO_2 = NaHCO_3 + NH_4^+ + Cl^-$
(2) $2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$

Reaction (1) depends upon the slight solubility of sodium bicarbonate in the solution at a temperature of 15° C. or below. The reaction is carried out by first saturating the brine with ammonia, and then with carbon dioxide. Following this the solution is cooled and the bicarbonate removed by filtration. Reaction (2) takes place upon gentle ignition.

The success of the process depends upon the recovery of the ammonia by the reaction: $2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O$. Limestone serves as the source of both the carbon dioxide and the lime: $CaCO_3 = CaO + CO_2$.

The phase relations of the various hydrates are indicated in Figure 1. The anhydrous salt is known commercially as **soda-ash** and the decahydrate as **washing soda.** As the salt of a weak acid, sodium carbonate is hydrolyzed in solution, $1N$ Na_2CO_3 containing about $0.01N$ OH^-; and many of its uses, such as washing, depend upon this property. As a salt of a weak acid, it is also used to neutralize strong acids and in the preparation of their sodium salts. The consumption of sodium carbonate by various industries is given in Table IV.

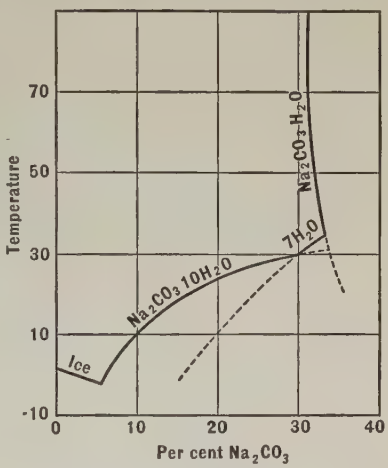


FIG. 1.—The system sodium carbonate and water.

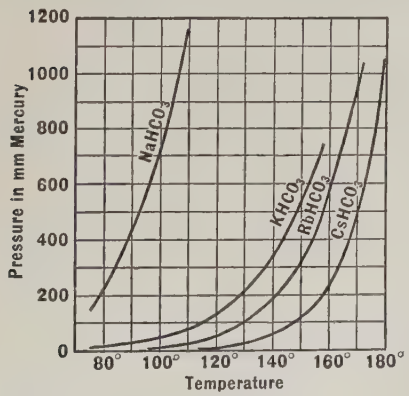


FIG. 2.—Decomposition pressures of alkali bicarbonates.

Sodium bicarbonate, the common household baking soda, is obtained as a step in the Solvay process. With the exception of lithium, the alkali bicarbonates are all more insoluble than the carbonates. The conversion of bicarbonate to carbonate by heating becomes more difficult the higher the atomic weight of the alkali, as is indicated in the plot of decomposition pressures (Fig. 2). Advantage may be taken of the reversible reaction, $CO_3^= + CO_2 + H_2O = 2HCO_3^-$, to convert carbonates into bicarbonates. When a bicarbonate solution is evaporated at 100° or above, sodium sesquicarbonate, $Na_3(CO_3)(HCO_3) \cdot 2H_2O$ separates.

The bicarbonate is employed in baking, the use depending upon the liberation of carbon dioxide with acid, as does also its use in certain types of fire extinguishers. The ease of purification of sodium bicarbonate by crystallization renders it a valuable standard in the titration of acids and bases. For this use it is fused to convert to the carbonate and to remove the last traces of water. This operation should be carried out in an atmosphere of CO_2, since the decomposition pressure of Na_2CO_3 is 2.2 mm. at 700° and 6.2 mm. at 1,000°.

14. Potassium Carbonates.—For centuries potassium carbonate was extracted from wood ashes; hence its name, potash. It may be made from the chloride by the Le Blanc process, but not by the Solvay process, since the bicarbonate is not sufficiently insoluble. However the conversion is generally carried out: (1) by the precipitation of $KHCO_3 \cdot MgCO \cdot 4H_2O$ by passing CO_2 under pressure into a suspension of $MgCO_3$ in KCl solution and (2) the recovery of the potassium carbonate from the double salt by decomposition with hot water giving insoluble $MgCO_3$ and a solution of potassium carbonate, $2MgKH(CO_3)_2\text{-}4H_2O = 2MgCO_3 + K_2CO_3 + CO_2 + 9H_2O$. Other sources are the mother liquors obtained in the manufacture of beet sugar, wine-lees, and water used in washing crude wool which contains potassium fatty acids. In each case the organic material is ignited to give the carbonate.

Potassium carbonate crystallizes as the dihydrate. It is used in making soap and hard glass, and in the dyeing industries.

Potassium bicarbonate is similar in chemical properties to the sodium salt but is about three times as soluble.

15. Lithium, Rubidium, and Cesium Carbonates.—Lithium carbonate is the most important commercial compound of that element, and is used in medicine and in the preparation of other lithium compounds. Its solubility is sufficiently low so that it may be prepared by precipitation from a solution containing lithium ion by the addition of sodium carbonate. Lithium bicarbonate is soluble.

The rubidium and cesium carbonates and bicarbonates resemble the potassium compounds.

16. Fluorides.—The alkali fluorides do not occur free in nature to any large extent, although sodium aluminum fluoride, Na_3AlF_6, cryolite, occurs in large deposits. The fluorides are usually

prepared by the action of hydrofluoric acid upon the carbonate. With excess of the acid they tend to form acid fluorides such as MHF_2 or even MH_3F_4 (cf. **X—10**). These acid compounds are sometimes used as a method of preparing pure hydrogen fluoride, since they readily decompose with the evolution of the gas. Lithium fluoride is but slightly soluble. Sodium fluoride has some use as an insecticide and a wood preservative. It is also used in the preparation of complex fluorides.

17. Chlorides.—Alkali chlorides are found in great deposits resulting from the evaporation of inland lakes or seas.

Sodium chloride. In many places great beds of almost pure sodium chloride have been located and from these salt is taken by ordinary mining operations. In regions removed from naturally occurring salt deposits, sodium chloride is obtained from sea water or salt wells usually by solar evaporation in shallow ponds. Crude salt generally contains traces of calcium and magnesium chlorides which are objectionable because of their deliquescence. Pure sodium chloride may be precipitated from a concentrated brine upon addition of hydrogen chloride gas, due, in part, to the increase in concentration of chloride ion. The reaction qualitatively is that predicted by the Mass Law.

The solubility of sodium chloride changes but slightly with temperature, being 26.3 per cent at 0° and 28.1 per cent at 100°. Phase relation in the salt-water system are given in Figure 3. The crystal structure has been discussed in Paragraph **6.**

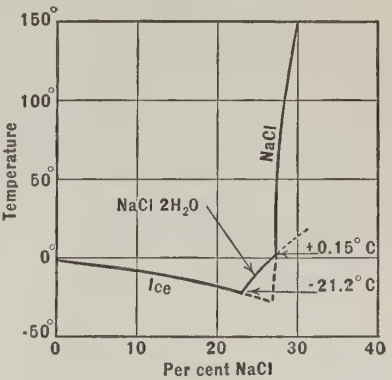


Fig. 3.—The system sodium chloride and water.

The production of salt in the United States in 1926 was about seven million tons. Of this a million and a half tons were used in the preparation of the carbonate by the Solvay process. Other important industrial uses include refrigeration; agriculture; household; metallurgy of silver, copper, and lead; tanning; preservative; ceramics; salting out of soap; preparation of hydrochloric acid and sodium sulphate by reaction with

sulfuric acid; and the preparation of sodium hydroxide and chlorine by electrolysis. Each of the two latter industries employs approximately 150,000 tons yearly.

18. Potassium Chloride.—For many years Germany enjoyed an almost complete monopoly of potassium salts through the possession of the extensive deposits of chloride at Stassfurt in Prussia, but recently important deposits have been developed in Alsace, France.

The major portion of the potassium chloride of the Stassfurt deposits is in the form of double salts of magnesium and calcium chloride, sulphate, and borate. The most important of these is carnallite, $MgCl_2 \cdot KCl \cdot 6H_2O$, and to a lesser extent kainite, $MgSO_4 \cdot KCl \cdot 3H_2O$. Potassium chloride is extracted by dissolving carnallite in hot magnesium chloride solution; cooling this solution precipitates the greater part of the potassium chloride. The yearly production of potassium chloride at Stassfurt is in excess of 1,500,000 tons. The dust from blast furnaces manufacturing pig iron, and the dust from cement kilns, has been shown to contain potassium chloride and also sulphate in recoverable amounts. It is estimated that the United States could produce several hundred thousands of tons yearly from this source. The most important uses of the potassium chloride are as fertilizer and in the production of potassium hydroxide and other potassium compounds.

19. Lithium, Rubidium and Cesium Chlorides.—Lithium chloride is the most soluble of the group. It forms mono-, di-, and tri-hydrates, and in many respects resembles magnesium chloride.

One of the most important sources of rubidium and cesium chlorides is the mother liquor remaining after the extraction of the potassium chloride from carnallite. These elements are usually separated from the liquid by conversion into the relatively insoluble alums through the addition of aluminum sulphate.

20. Bromides and Iodides.—Bromides and iodides occur in sea water and in the various salt deposits. They are not recovered as such, but the halogens are liberated as the free elements, and the salts prepared from the elements by methods discussed under the halogens. Sodium and potassium bromides are used in medicine as sedatives, and in photography for precipitating silver bromide and as retardants in developers. The

alkali iodides find limited application in photography, and in medicine to supply iodine to the thyroid gland, and sometimes in tincture of iodine, to increase the amount of iodine that can be dissolved.

21. Cyanides.—Sodium cyanide is made on a large scale from sodium amide (Table III) by reduction with carbon at red heat: $NaNH_2 + C = NaCN + H_2$. A mixture of sodium and potassium cyanides may be prepared by the reduction of potassium ferrocyanide with sodium: $K_4Fe(CN)_6 + 2Na = 4KCN + 2NaCN + Fe$. Potassium cyanide is also manufactured by the action of ammonia upon a mixture of potassium carbonate and carbon at a high temperature: $K_2CO_3 + 2NH_3 + 4C = 2KCN + 3CO + 3H_2$. The alkali cyanides are very soluble in water, and the solution is quite alkaline due to the hydrolysis of the cyanide. The uses of these compounds in gold mining and electroplating depends upon the formation of complex cyanides with gold, silver and platinum. The sodium salt is now generally used due to the fact that it is cheaper and gives a higher weight of cyanide per pound of salt. Like all substances giving cyanide ion or hydrogen cyanide in solution, these salts are very poisonous.

22. Sulfates.—The alkali sulphates and double sulphates with calcium and magnesium are found in the various salt lakes and salt deposits. Double sulphate of sodium and potassium, as $KNaSO_4$, and various types of sodium and potassium alums are of frequent occurrence in volcanic lava. Some potassium sulphate is extracted from the Stassfurt deposits.

Sodium sulphate is used in medicine as a cathartic and in the manufacture of cheap glass to furnish the sodium. It can be crystallized as $Na_2SO_4 \cdot 10H_2O$, Glauber's salt, below 32.384°, and as the anhydrous sulfate above that temperature. The transition point serves as a convenient "fixed point" in the standardization of thermometers. The solubility of the decahydrate increases rapidly with temperature and the solutions formed at the higher temperatures may be readily cooled in the supersaturated state. If a particle of this solid hydrate is then added, crystallization takes place and the whole solution appears to solidify. An unstable heptahydrate may be crystallized out below 24° C. Potassium sulphate is used in the preparation of potassium alum and also as fertilizer, being preferred to the chloride for this purpose with certain crops, especially tobacco.

23. Nitrates.—Alkali nitrates are formed in nature through the decomposition of organic material. Due to the solubility of these salts, deposits are found only in the rainless regions of the earth. By far the most important occurs in Chile, and is composed chiefly of sodium nitrate. Commercial "Chile saltpetre," consisting of 95 to 98 per cent sodium nitrate, is made by extracting the crude nitre rock with water. Approximately a million tons of sodium nitrate are used each year for fertilizer and in the manufacture of nitric acid. Chile saltpetre was formerly almost the only source of the nitric acid and nitrates of industry, but is now being replaced by the various processes for the fixation of atmospheric nitrogen (cf. **XII—32**).

The uses of the alkali nitrates which depend upon the oxidizing power of nitrate are discussed under the chemistry of nitrogen. Potassium nitrate absorbs water less readily than sodium nitrate, and for this reason was formerly used more extensively than the sodium salt in gunpowder. Potassium nitrate is prepared from the sodium by double decomposition with potassium chloride, taking advantage of the fact that the solubilities of potassium chloride, potassium nitrate and sodium nitrate increase rapidly with temperature, while that of sodium chloride is hardly affected. The sodium nitrate is dissolved in hot water and concentrated potassium chloride solution is added, whereupon most of the sodium is precipitated as chloride. The solution is then evaporated, more sodium chloride first separating, followed by potassium nitrate.

The crystal structure of sodium nitrate is similar to the simple cubic arrangement of sodium chloride (Par. **6**), the nitrate group as a whole occupying the positions corresponding to the chloride ion. The alkali nitrates differ from the nitrates of most of the other metals in that upon heating they first decompose into nitrite and oxygen. Upon further heating nitrogen and oxygen are evolved and the oxide and peroxide formed. A mixture of 45 per cent sodium and 55 per cent potassium nitrates melts at 220° and is a convenient high temperature liquid bath.

24. Other Salts of the Alkali Metals.—Compounds of the alkali metals with sulphide, thiosulfate, chlorate, perchlorate, phosphate, borate, and silicate are of importance, but since their properties and uses depend so largely upon the chemistry of

negative ions, they are discussed in the chapters dealing with those ions.

25. Chemical and Analytical Properties of Ions.—The outstanding characteristic of the alkali ions is the slight tendency to form insoluble salts or complex ions. As already mentioned, lithium resembles the alkaline earth metals in many respects. Thus lithium fluoride, carbonate, and phosphate are moderately insoluble and the bicarbonate more soluble than the carbonate, like the alkaline earth metals, and unlike the rest of the alkalies. Lithium ion is slightly hydrolyzed. The chloroplatinates, acid tartrates, and alums of lithium and sodium are soluble, while the corresponding salts of potassium, rubidium, and cesium are relatively insoluble. Potassium forms with sodium cobaltinitrite in dilute acid the precipitate, $K_2NaCo(NO_2)_6$. It is the least soluble of the potassium compounds, but this does not serve to distinguish potassium from rubidium, cesium, or ammonium, which form corresponding compounds. Potassium picrate, $C_6H_2(NO_2)_3OK$, potassium perchlorate, $KClO_4$, and sodium and potassium fluosilicates, Na_2SiF_6, K_2SiF_6, are also but slightly soluble. Sodium pyroantimonate, $Na_2H_2Sb_2O_7$, is the least soluble of the sodium salts.

Potassium ion appears to be more readily absorbed than sodium ion, and this in part accounts for the much smaller quantity of potassium salts in sea water, although another factor may be its more ready precipitation as an iron silicate, $KFeSi_2O_6$.

In the quantitative analysis of the alkalies, they are usually converted to the chlorides and the mixture weighed. The lithium chloride may be extracted by dissolving in amyl alcohol. Potassium, rubidium, and cesium are converted to the chloroplatinates and the sodium obtained by difference. Although rubidium and cesium are rarely present in quantity they may be separated from potassium by taking advantage of difference in solubility of the acid tartrates.

In addition to the use of the spectroscope in the identification of the alkalies, advantage is taken of the color imparted to the Bunsen flame by the presence of volatile compounds of these elements. Lithium colors the flame red, sodium yellow, potassium violet, rubidium bluish red, and cesium blue. The sodium flame test is of extraordinary delicacy, being capable of detecting 10^{-10} grams of sodium. Since this quantity of sodium is present

in practically every substance, it is necessary in making a flame test for sodium to judge the amount of sodium present largely by the length of time that the intense yellow color persists in comparison to pure sodium chloride as a standard. The potassium flame test is about five thousand times less sensitive than the sodium test. In the presence of any considerable amount of sodium it is necessary to use a thick blue glass to cut out the yellow sodium light in order to detect the potassium.

CHAPTER V

GROUP II. ALKALINE EARTH METALS

1. On the basis of their atomic structure the elements with two valence electrons may be divided into a main group consisting of beryllium (formerly often called glucinium from the sweet taste of some of its compounds), magnesium, calcium, strontium, barium, and radium, and a subgroup, zinc, cadmium, and mercury. As a common characteristic the main group elements have kernels with the same number and arrangement of electrons as the preceding noble gas, while the subgroup elements have kernels with eighteen electrons in the outer shell. Beryllium and magnesium are smaller and much less basic than the rest of the main group, and before the fundamental differences in atomic structure were recognized, they were frequently classified with the subgroup elements. The remaining elements of the main group have hydroxides with distinctly alkaline properties and have long been known as the alkaline earth elements, and we shall use the term as applying to all of the main group.

2. Physical Properties of Metals.—The elements in the free state are highly metallic. They have grey white luster when freshly cut, but readily tarnish, especially the heavier members of the group. Although somewhat brittle, they may be hammered and rolled. Beryllium is hard enough to scratch glass, while barium is but slightly harder than lead. The metals are good electrical conductors; the specific conductivity of calcium is about 45 per cent that of silver. Their melting points (Table I) are much higher than those of the alkali metals.

3. Chemical Properties.—In all of their compounds the elements exhibit a valence of + 2, i.e. both of the two outer electrons are always lost when the elements enter into chemical reactions. It will be observed (Table I) that the oxidation potential of the heavier members of the group is as great as that of the alkali metals. Thus barium readily reacts with water losing its electrons to the hydrogen of the water and forming barium ion and molecular hydrogen: $Ba + 2H_2O = Ba^{++} + 2OH^- + H_2$. The mechanism of the reaction involves taking the two electrons

away from the barium and this, as given in Table I, requires about five volts for the first electron and ten for the second. These values of the ionization potentials are higher for the

TABLE I

ATOMIC AND PHYSICAL PROPERTY OF ALKALINE EARTH ELEMENTS

	Be	Mg	Ca	Sr	Ba	Ra
Atomic number	4	12	20	38	56	88
Atomic weight	9.02	24.32	40.07	87,63	137.37	225.95
Isotopes	none	24,25,26	40,44	88,86	138,136	224,226
Electrons in various quantum levels, 1st	2	2	2	2	2	2
2d	2	8	8	8	8	8
3d		2	8	18	18	18
4th			2	8	18	32
5th				2	8	18
6th					2	8
7th						2
Ionic radius $\times 10^8$ cm. (if $Cl^- = 1.81$)	0.31	0.65	0.99	1.13	1.35	
Ionization potential of gaseous atom, volts, 1st electron	9.5	7.61	6.09	5.67	5.19	5
2d electron	18.1	14.97	11.82	10.98	9.96	
Potential between metal and molal solution of ion, $M = M^{++} + 2E^-$ in volts	+ 1.69	+ 2.40	+ 2.87	+ 2.92	+ 2.90	
Heat of hydration of gaseous ions, kg. cal. approx.		460	395	355	305	
Melting point ° C	1,350	651	810	800	850	(960)
Boiling point ° C	(1,500)	1,110	1,170		1,140	
Density of metal	1.85	1.75	2.55	2.6	3.75	6.0

alkaline earth metals than for the alkali metals, and the reason that barium is so readily oxidized to form the ion is to be found in the large heat of hydration of the barium ion. However, the rate of reaction of the second group elements with water is much slower than that of the alkali metals, even in the case of the more electropositive members; and magnesium and beryllium are scarcely attacked by water alone at ordinary temperatures. The metals burn brilliantly when heated in air or oxygen, forming the monoxide, except in the case of barium, which forms the peroxide. A certain amount of the nitride is also formed when burned in air, especially with magnesium, calcium, and

radium. At low temperatures the metal surfaces are protected from rapid oxidation by oxide films; this is particularly true of beryllium and magnesium. Beryllium does not dissolve with appreciable speed in water even when boiled. Magnesium evolves hydrogen very slowly with cold water, while with calcium a slow stream of bubbles is observed. The metals all dissolve rapidly in acids. Beryllium dissolves in the alkali hydroxides in a manner similar to aluminum: $Be + OH^- + H_2O = HBeO_2^- + H_2$. Due to their action as strong reducing agents the metals are oxidized by many of the negative elements. A summary of the more important types of reactions is given in Table II.

TABLE II

Reactions of Group II Metals

$2M + O_2 = 2MO$	Ba also forms BaO_2
$M + 2H_2O = M(OH)_2 + H_2$	Very slow with Be and Mg
$M + H_2 = MH_2$	With Ca, Sr, and Ba at high temperature
$M + 2H^+ = M^{++} + H_2$	
$4M + 10H^+ + NO_3^- = 4M^{++} + NH_4^+ + 3H_2O$	With dilute acid: H_2 also evolved
$M + X_2 = MX_2$	X_2 = any halogen
$3M + N_2 = M_3N_2$	High temperature
$3M + 2NH_3 = M_3N_2 + 3H_2$	Heated
$M + S = MS$	Also with Se and Te
$M + 2C = MC_2$	Especially with Ca, Sr. High temperature
$3M + 2P = M_3P_2$	Heated

4. Occurrence.—None of the elements of the group exist free in nature. Beryllium compounds do not occur abundantly but small quantities are found in many minerals and granitic rocks, usually as complex silicates and aluminates. The most important mineral is beryl, $3BeO \cdot Al_2O_3 \cdot 6SiO_2$. Colored dark green with chromium it is known as emerald. Masses of beryl weighing more than a ton have been found in New Hampshire. With the exception of radium, the other members of the group are more abundant. Their occurrence as per cent of the earth's crust is estimated as: magnesium 2.24, calcium 3.47, strontium 0.02, barium 0.08. They are found in combination with practically all of the acid oxides. A few of the more important minerals are: magnesite, $MgCO_3$; talc or soapstone, $H_2Mg_3(SiO_3)_4$; asbestos, $CaMg_3(SiO_3)_4$; dolomite, $MgCO_3 \cdot CaCO_3$; spinel,

$Mg(AlO_2)_2$; carnallite, $MgCl_2 \cdot KCl \cdot 6H_2O$; limestone, $CaCO_3$; gypsum, $CaSO_4 \cdot 2H_2O$; fluorspar, CaF_2; apatite, $Ca_5(PO_4)_3X$, (X = Cl or F); strontianite, $SrCO_3$; barites, $BaSO_4$. Magnesium and calcium chlorides and sulfates are present in sea water the former in somewhat larger concentrations. Both elements are found as integral parts of animal and vegetable matter, although calcium is more prevalent than magnesium.

Radium is widely distributed in almost all rocks but in extremely small quantities. Primary uranium minerals contain about 3.4×10^{-7} grams of radium per gram of uranium (cf. **XXII—3**).

5. Metals: Preparation and Uses.—The metals are generally prepared by the electrolysis of their molten chlorides or fluorides to which alkali halides have been added to decrease the melting point. The oxides or hydroxides cannot be used because of their high melting points, although magnesium is now being manufactured by the electrolysis of a molten solution of the oxide in fluoride similar to the process for aluminum (cf. **VI—14**). Calcium is prepared by the electrolysis of a mixture of the chloride and fluoride in a graphite crucible, which acts as the anode. The cathode is an iron rod just dipping into the molten salts. The liberated calcium adheres to the rod which is slowly raised, thus forming a long "stalk" of calcium. The metals are difficult to prepare by reduction with chemical agents; however, beryllium and magnesium chlorides may be reduced by sodium or potassium at high temperatures, and barium oxide is reduced by silicon at 1,200°.

Magnesium is the only metal of the group of any considerable commercial importance at present. It is employed in signal flares and in photographic flash lights, usually in the form of powder; the latter use depends upon the high proportion of ultraviolet light in the flame formed by the combustion of the metal. It is also made into ribbon, the major part of which is now used in the degasification of radio tubes. Its importance in this connection is due to the absorption by the heated metal, not only of oxygen, but also of nitrogen through the formation of the nitride, Mg_3N_2. It is employed as a deoxidizer in casting bronze, nickel-silver, and monel metal. A small per cent of magnesium added to aluminum greatly increases the ease of machining of the latter, and the aluminum alloy, **magnalium**,

is important because of its low density and high tensile strength. Beryllium would doubtless be useful in the manufacture of light alloys if it were more abundant.

Radium amalgam is formed upon the electrolysis of radium chloride solution using a mercury cathode. The mercury may be driven off by heating to leave the radium. The metal is said to blacken quickly due to the formation of the nitride.

Compounds

6. Oxides.—The monoxides are difficultly fusible (Table III) and extremely stable, remaining undecomposed at temperatures of 3,000° C. Their heats of hydration increase in order of the atomic weights.

TABLE III

Oxides of Group II

	BeO	MgO	CaO	SrO	BaO
Common name	beryllia	magnesia	lime	strontia	baryta
Melting point ° C	2,450	2,800	2,570	2,700	2,000
Heat of formation kg. cal. per mole	135.9	143.9	151.9	141.2	133.4
Heat of hydration $MO + H_2O = M(OH)_2$		5.4	15.1	17.7	22.3
Solubility moles/liter of $M(OH)_2$ at 20° C	5×10^{-9}	3×10^{-4}	0.022	0.065	0.22
Decomposition temp. ° C. $M(OH)_2 = MO + H_2O$ (gas 1 at.)			547	778	998

Beryllium oxide is as hard as corundum but the heavier oxides are soft. Beryllium oxide does not react with water. Magnesium oxide, if not ignited too strongly, reacts very slowly, while the rest of the group react rapidly. With lime the hydration reaction is called "slaking." The reaction starts slowly, but the heat evolved soon raises the temperature to a point where the reaction proceeds rapidly. The heat of slaking is sufficient, under some conditions, to cause the ignition of wood or other combustive material; hence the accidental slaking of stored lime often results in destructive fires.

The solid oxides crystallize in the sodium chloride type of ion lattice, with the exception of beryllium oxide, which is similar to zinc oxide (Append. V). The oxides are extremely poor conductors of heat.

The oxides of all except beryllium are generally prepared by the decomposition of the carbonates. The ease of decomposition decreases with increasing atomic weight, that is with increasing basicity of the metal oxide. The manufacture of lime is carried out in tall chimney-like furnaces known as lime kilns. The process is continuous; limestone is fed into the top, is heated and decomposed by a draft of hot gas, and the lime is removed at the bottom of the kiln. The reaction is carried out at as low a temperature as possible to prevent the fusion of silicates present in the limestone which would render the lime inactive. In order to keep the temperature low the partial pressure of the carbon dioxide must also be kept low. In Figure 1 are given the pressures of carbon dioxide in equilibrium with the oxide and carbonate at various temperatures. If calcium carbonate is heated in a retort under atmospheric pressure it requires a temperature of 910° C. to bring about decomposition; however, in the operation of the lime kiln the blast of hot gases through the furnace keeps the partial pressure of the carbon dioxide at a low figure and permits the reaction to go to completion at temperatures much below 910°. In the case of barium carbonate, the decomposition temperature is so high that carbon is mixed with the charge further to lower the partial pressure of the carbon dioxide: $C + CO_2 = 2CO$. Barium oxide is sometimes prepared from the nitrate, since it decomposes at much lower temperatures.

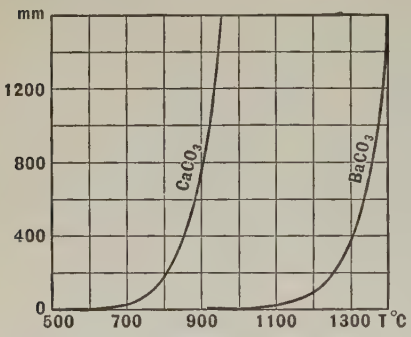


FIG. 1.—Decomposition pressures of calcium and barium carbonates.

Magnesia in the form of bricks is used for lining furnaces and other refractory purposes. Mixed with asbestos it is employed as heat insulation for hot water and steam pipes. Other uses include: the manufacture of Sorel cement (Par. 9); absorbent in the manufacture of dynamite; vulcanization of rubber; adulterant of paint. Large quantities of mixed magnesium and calcium oxides are used for some purposes in place of pure magnesia, the mixture being produced by the calcination of dolomite.

The production of lime in the United States in 1925 was 4,500,000 tons. This was consumed chiefly in making the hydroxide (*vide infra*). Heated in the oxy-hydrogen flame, lime gives out an intense light, hence its former use in the "lime light." Calcium oxide is often employed as a dehydrating agent, for example, in the preparation of absolute alcohol and the drying of ammonia gas. A mixture of sodium hydroxide and calcium oxide, "soda-lime," is often employed to remove both water and carbon dioxide from gases. Lime containing more than 5 per cent magnesium oxide does not slake readily and is called "lean."

Barium oxide is the only one of the group which may be converted into the **peroxide,** BaO_2, upon heating in air, although with the exception of beryllium the peroxides may all be prepared by the action of hydrogen peroxide upon the metal ion. Barium peroxide is mentioned in connection with the preparation of oxygen and hydrogen peroxide. With water it readily forms the hydrate, $BaO_2 \cdot 8H_2O$. It may be pointed out that the tendency to form peroxides appears to be related to the size of the positive ion. Thus barium being most like the alkalies in this respect shows greatest similarity in the formation of the peroxide.

7. Hydroxides.—The formation of the hydroxides from oxides has been discussed above. The alkaline reaction of the hydroxides is limited by their solubilities (Table III); however the hydroxides of calcium and the heavier members of the group may be classed as strong bases. Their salts with strong acids are very slightly hydrolyzed. Barium hydroxide is the only one which is stable enough to be heated to fusion.

Beryllium hydroxide is amphoteric (Hildebrand, *Princ. of Chem.*, p. 194), a fact which is not surprising in view of the very small size of Be^{++} (cf. **III—7**). It thus dissolves in both acids and bases: $Be(OH)_2 + 2H^+ = Be^{++} + 2H_2O$, and $Be(OH)_2 + OH^- = HBeO_2^- + H_2O$. The beryllate solution is unusual in one respect, in that upon heating the solution the hydroxide is precipitated in a form which is less soluble than the hydroxide precipitated from Be^{++} and OH^-.

Some **magnesium hydroxide** is prepared by the action of steam upon magnesium chloride: $MgCl_2 + H_2O = MgO + 2HCl$. The hydroxide is precipitated from a solution of magnesium ion

upon the addition of a strong base. It belongs to the class of sparingly soluble bases which are soluble in excess of ammonium ion: $Mg(OH)_2 + 2NH_4^+ = Mg^{++} + 2NH_4OH$.

Because of its low cost of production, **calcium hydroxide** is used commercially in many processes requiring hydroxide ion. A suspension of the solid in its saturated solution (milk of lime) is often employed. Among the more important uses are: the preparation of mortar, bleaching powder, ammonia, alkali hydroxide; purification of sugar and illuminating gas; removal of hair from hides; softening of water (Par. 11). The most extensive use is that in **mortar.** This is made by mixing slaked lime, one volume, with sand, three or four volumes, and water to make a thick paste. The mortar gradually hardens due, first, to the evaporation of water and the cementing action of the deposited hydroxide, and second, to the absorption of carbon dioxide from the air: $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$. There follows a very slow formation of calcium silicate. The setting is accompanied by a decrease in volume but the presence of the large amount of sand prevents a large total shrinkage and renders the product porous.

Strontium hydroxide is made by heating the carbonate in steam: $SrCO_3 + H_2O = Sr(OH)_2 + CO_2$. This reaction takes place at a lower temperature than the reaction: $SrCO_3 = SrO + CO_2$, due in part to the lowering of the partial pressure of the carbon dioxide by the steam, and in part to the energy of formation of the hydroxide from the oxide. The hydroxide crystallizes as $Sr(OH)_2 \cdot 8H_2O$. Strontium hydroxide is employed in the refinement of sugar to recover sugar from dilute solutions. Both calcium and strontium ions form insoluble precipitates (saccharates) with sugar from hydroxide solutions, and these may be decomposed by the action of carbon dioxide. This property is utilized in sugar refining.

Barium hydroxide crystallizes with eight molecules of water. Its solution is known as "baryta-water," and is often employed as a standard alkali in quantitative analysis. The insolubility of the barium carbonate keeps the solution free from carbonate ion, which is usually present in sodium hydroxide and which is objectionable in titrating acids when certain indicators are used.

8. Carbonates.—Normal beryllium carbonate does not exist, but a basic carbonate is precipitated upon the addition of sodium

carbonate to a soluble beryllium salt (Hildebrand, *Princ. of Chem.*, p. 201). The precipitate is soluble in excess of the reagent due to the formation of the beryllate ion, $HBeO_2^-$.

Normal magnesium carbonate, $MgCO_3$, occurs in nature as the mineral, magnesite. A basic carbonate, $Mg_4(OH)_2(CO_3)_3 \cdot 3H_2O$, is precipitated when an alkali carbonate is added to magnesium ion. The precipitate is soluble in excess ammonium ion due to the equilibria: $NH_4^+ + OH^- = NH_4OH$, and $NH_4^+ + CO_3^{--} + H_2O = HCO_3^- + NH_4OH$. The carbonate is also soluble in carbonic acid (see Calcium Carbonate below). The precipitated basic salt is used in medicine under the name "magnesia alba," partly as a mild alkali and partly for the physiological action of magnesium ion. Considerable quantities are consumed in the preparation of tooth powder and of silver polish. The natural carbonate and also the double carbonate with calcium, dolomite, $CaCO_3 \cdot MgCO_3$, are used for the commercial production of carbon dioxide. The compound $MgCO_3 \cdot (NH_4)_2CO_3 \cdot 4H_2O$ is precipitated upon the addition of ammonium carbonate to magnesium ion in a solution containing 30 per cent alcohol. Advantage is taken of this fact in qualitative analysis.

Calcium carbonate crystallizes in two forms, calcite, rhombohedral, and aragonite, rhombic. The latter is unstable in respect to the former but the rate of transition is slow at ordinary temperatures. The heat of transition is about 300 cal. per mole. The carbonate is the most abundant of the calcium compounds. The most common forms are: Iceland spar, which is almost pure calcite; marble; limestone, which is less crystalline and contains clay and other silicates; chalk, which has been formed from the shells of minute marine organisms; shells and pearls.

The crystal structure of calcite is similar to that of sodium chloride, with the carbonate group replacing the chloride. The three oxygens are symmetrical about the carbon. Calcite is luminescent under the action of cathode rays. The glow persists for some time after the action of the rays has been stopped.

Calcium carbonate is precipitated upon the addition of carbonate ion. If the solution is boiling the precipitate is largely aragonite; in the cold it is finely divided calcite, which becomes coarse grained and distinctly crystalline upon standing. The solubility of calcium carbonate is increased in the presence of hydrogen ion due to the equilibrium, $H^+ + CO_3^{--} = HCO_3^-$

(cf. **XIII—10**) and hence, $CaCO_3 + H^+ = Ca^{++} + HCO_3^-$. With excess acid, carbon dioxide is, of course, liberated. Due to the fact that the second ionization step of carbonic acid is much less than the first, calcium carbonate dissolves in carbonic acid: $CaCO_3 + H_2CO_3 = Ca^{++} + 2HCO_3^-$. This reaction occurs wherever water comes in contact with rock or soil containing calcium (or magnesium) carbonate, and imparts "hardness" to the water, which is objectionable for certain purposes (Par. **10**). The bicarbonate solution upon heating loses carbon dioxide and the carbonate is again precipitated. Stalactites and stalagmites are formed in caves by the precipitation of calcium carbonate brought about by the loss of carbon dioxide from water, which has been highly charged with the gas and thereby dissolved large quantities of limestone.

In addition to widespread use as building material, limestone is used in the manufacture of cement, lime, and glass. It is used in many metallurgical processes to form a flux with silica through the formation of calcium silicate.

Strontium and barium carbonates occur in nature as strontianite, $SrCO_3$, and witherite, $BaCO_3$, respectively. Next to the sulfates, they are the most important sources of these elements. The stability of the carbonates toward decomposition into the oxides increases and the solubility in water decreases with increasing atomic weight. The general solubility equilibria of these carbonates with acid is similar to those of calcium, discussed above.

9. Halides.—The halides of beryllium, unlike most metallic halides, are very poor conductors of electricity in the fused state. The beryllium halides are highly hydrolyzed in solution, but not as much as the aluminum halides. The solutions upon evaporation yield basic salts.

The fluorides of the members of the group other than beryllium are insoluble in water, even in the presence of an excess of fluoride ion. The fluorides of calcium, strontium, and barium crystallize in ionic lattices of the so-called "calcium fluoride structure" (Append. V). Calcium fluoride occurs as the mineral fluorite or fluor-spar, and is important as the chief source of fluorine compounds. It is unusually transparent to ultra-violet light, nearly to 0.1 μ.

The occurrence of magnesium chloride in salt deposits as

double salts has been mentioned (cf. **IX—18**). It crystallizes from its water solution at room temperature as $MgCl_2 \cdot 6H_2O$. This hydrate also occurs as the mineral, bischofite. The anhydrous salt cannot be prepared from the hydrate, as upon heating it loses hydrogen chloride: $MgCl_2 + H_2O = MgO + 2HCl$. This reaction may be employed for the manufacture of hydrochloric acid. Magnesium chloride combines with the oxide to form a basic chloride, Mg_2OCl_2. The heat of the reaction, 20 kg. cal., indicates that the compound is very stable. This reaction is the basis for the **Sorel cement** which is now used extensively as a substitute for tile. Magnesium chloride is often present in table salt, and due to its deliquescent nature causes the salt to "cake" in damp weather. This may be avoided by the addition of enough sodium bicarbonate to form the basic magnesium carbonate.

A number of double compounds of calcium chloride occur as minerals, for example, tachydrite, $CaCl_2MgCl_2 \cdot 12H_2O$, and apatite, $Ca_5(PO_4)_3Cl$ (or $Ca_5(PO_4)_3F$). The chloride may also be recovered from natural brines and salt deposits. Below 30° the salt crystallizes as the hexahydrate. Upon heating it may be dehydrated to form successively tetra-, di-, and monohydrates, and anhydrous salt. The latter contains some oxides formed through the loss of hydrogen chloride, as in the case of magnesium chloride discussed above. The solubility relations of the various hydrates are given in Figure 2. The eutectic of the hexahydrate and ice is — 55° C. The anhydrous salt and dihydrate are used extensively as drying agents. The equilibrium pressure of water vapor for the reaction, $CaCl_2 \cdot 2H_2O + 2H_2O = CaCl_2 \cdot 4H_2O$, is 0.92 mm. at 0°, and 3.78 mm. at 20°. Calcium chloride forms compounds with ammonia, $CaCl_2 \cdot 8NH_3$, and with alcohol, $CaCl_2 \cdot 4C_2H_6O$, and hence cannot be used for drying these substances; nor

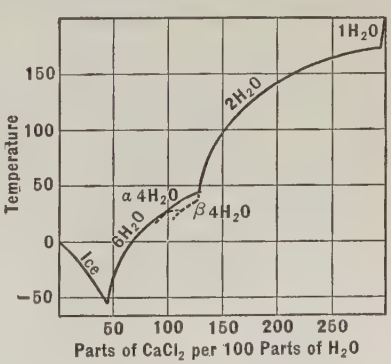


FIG. 2.—The system calcium chloride and water.

can it be used to dry hydrogen sulfide, which it decomposes somewhat with the evolution of hydrogen chloride.

The deliquescence of calcium chloride and its low cost make it useful in sprinkling roads. Its high solubility and the low freezing point of its solutions render it useful in refrigerating brines. Its principal commercial sources are ammonia recovery plants, $2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O$ (see Ammonia **XII—6**) and the Solvay soda process (cf. **IV—13**), in both of which it results as a by-product.

Barium chloride is prepared for use as an analytical reagent by heating a mixture of barium sulfate, calcium chloride, and carbon: $BaSO_4 + CaCl_2 + 4C = BaCl_2 + CaS + 4CO$. The chloride is leached out and purified by recrystallization.

Radium is frequently prepared for commercial use in the form of chloride. Both the chloride and bromide are more insoluble than the corresponding barium compounds.

In general the solubilities of the alkaline earth halides increase in order of increasing atomic weight of the halogen, and decrease with increasing atomic weight of the metal.

10. Sulfates.—Beryllium sulfate is very soluble, and forms syrupy liquids from which it is difficult to crystallize a pure compound. The tetra and hexahydrates have been obtained; the former is apparently unstable in respect to the latter.

Magnesium sulfate is found in many mineral waters and in the bittern of sea water. It occurs as the minerals kieserite, $MgSO_4 \cdot H_2O$, and epsomite (epsom salts), $MgSO_4 \cdot 7H_2O$. Between 1.8° and 48° the rhombic heptahydrate crystallizes from solution; below 1.8° a dodeca hydrate separates; and at higher temperatures there are formed a number of lower hydrates. The anhydrous salt cannot be prepared, due to formation of basic sulfates upon heating the hydrates. Magnesium sulfate is used in weighting and sizing cotton, silk, paper, and leather; in fireproofing fabrics; and in medicine as a purgative, and as a stimulant to increase the secretion of bile.

Calcium sulfate occurs in enormous deposits of **gypsum** $CaSO_4 \cdot 2H_2O$ (when pure white called alabaster); and less extensively as anhydrite, which is the anhydrous salt. The solid phase in equilibrium with the saturated solution is gypsum below 63.5° C., and anhydrite above (Fig. 3). The solubility of the two salts at the transition point is 0.03 moles per liter.

The solubility of anhydrite decreases rapidly with rising temperature and is only 0.005 moles per liter at 150° C. This decrease in solubility is partly responsible for the separation of boiler scale from water containing calcium sulfate (Hard Water, Par. 11). A second unstable and more soluble form of anhydrite also exists.

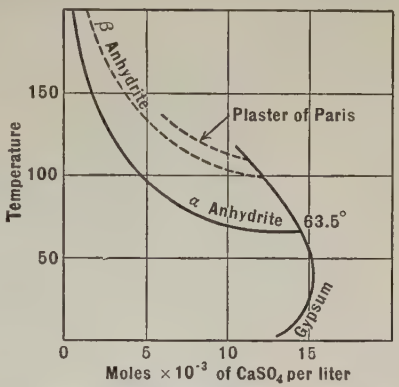


Fig. 3.—The system calcium sulfate and water.

Upon heating, gypsum loses water to form the hemihydrate: $2(CaSO_4 \cdot 2H_2O) = (CaSO_4)_2 \cdot H_2O + 3H_2O$. The equilibrium pressure of water vapor reaches one atmosphere at 107° C. The hemihydrate is known as plaster of Paris. When it is mixed with water the equilibrium is reversed, and the plaster sets to a mass of gypsum crystals. The setting results in an increase in volume, and the plaster thus fills perfectly any mold into which it may be poured. In making plaster of Paris the gypsum must not be heated too strongly, as the anhydrous salt is then formed which absorbs water very slowly. Such plaster is called "dead burnt." The largest use of sulfate is in the manufacture of plaster for the interiors of building. Two varieties of plaster are made: (1) cement plaster, which is plaster of Paris to which glue, glycerine, and other organic substances have been added as "retarders" to prolong the time of setting; and (2) hard finish plasters, such as Keenes cement, which is made by the calcination of the anhydrous sulfate with alum or borax. This second type of plasters sets very slowly, but gives a hard finish. Large quantities of sulfate are used in the manufacture of stucco and wall board and as a retarder for Portland cement (cf. **XIV—24**). The yearly consumption of gypsum in the United States is about six million tons.

Strontium sulfate, $SrSO_4$, celestite, and barium sulfate, $BaSO_4$, barite or heavy spar, are the most important minerals of these elements. These sulfates are extremely insoluble in water and dilute acids. They dissolve in concentrated sulfuric acid through the formation of HSO_4^-, and are reprecipitated upon dilution.

When the sulfate is treated with sodium carbonate solution, some of the sulfate is converted into carbonate: $BaSO_4 + CO_3^{--} = BaCO_3 + SO_4^{--}$. At equilibrium the ratio of the molal concentration of sulfate to carbonate for the barium salts is about 0.01. If barium sulfate is treated, for example, with 100 cc. of $M Na_2CO_3$, 0.2 grams of barium carbonate will be formed. By decanting the solution and repeating the treatment, any amount of the sulfate may be converted into carbonate. The sulfate may also be converted into soluble salts by reduction with carbon at about 800° to form the sulfide, which may then be dissolved in acid.

Barium sulfate is an important pigment. **Lithopone,** a mixture of barium sulfate and zinc sulfide, is prepared by the reaction: $BaS + ZnSO_4 = BaSO_4 + ZnS$. This pigment has excellent covering power and does not darken with hydrogen sulfide. Precipitated barium sulfate is also used as a pigment, especially as an adulterant of white lead, but its covering power is not good. Barium sulfate is further employed as a "filler" in wall paper and in glazed paper. It is taken internally in making X-ray photographs of the intestinal tract, on account of the opaqueness to X-rays of such a heavy atom as barium. The sulfate is the only barium salt which may be used, as it alone is sufficiently insoluble to prevent poisoning by the barium ion.

Radium sulfate is even more insoluble than barium sulfate. In the commercial extraction from uranium ores the sulfate is precipitated along with those of barium and lead, and converted into the chloride by either of the two methods discussed above.

11. Water Softening.—Water containing soluble calcium and magnesium salts is known as **hard water.** It is objectionable in the laundry because soap, which contains sodium or potassium salts of the higher fatty acids, such as stearic or palmitic acid, forms insoluble salts with calcium and magnesium. This results in a waste of soap and the precipitate is a slimy curd which is difficult to remove. Hard water is objectionable in boilers because of the formation of boiler scale. The negative ions present in hard water are principally chloride, sulfate, and bicarbonate. Upon heating to a high temperature much of the dissolved material is precipitated as scale which is composed largely of anhydrite (Par. 10), calcium carbonate, and magnesium oxy-compounds. Such scale is a very poor conductor of heat, and

its formation causes not only a waste of fuel, but also more rapid deterioration of the boiler through overheating at the surfaces where the heat is applied. Water which contains large quantities of bicarbonate may be softened simply by heating: $Ca^{++} + 2HCO_3^- = CaCO_3 + CO_2 + H_2O$. Such water is referred to as possessing **temporary hardness.** In many industrial plants water is softened by the addition of lime equivalent to the calcium bicarbonate present, and sodium carbonate equivalent to the additional calcium and magnesium: $2HCO_3^- + 2OH^- + 2Ca^{++} = 2CaCO_3 + 2H_2O$, and $Ca^{++} + CO_3^{--} = CaCO_3$.

In the **zeolite** or **"permutite" process** water is softened by filtering slowly through artificial or natural zeolite, which is a hydrated sodium aluminum silicate. Although the composition varies somewhat in the different forms, NaH_6AlSiO_7 may be written as an approximate formula. The sodium is replaceable by calcium, magnesium, ferrous and other divalent ions. $2NaH_6AlSiO_7 + Ca^{++} = Ca(H_6AlSiO_7)_2 + 2Na^+$. The equilibrium is reversible and when the efficiency of the zeolite drops, it may be regenerated by treating for a few hours with a concentrated solution of sodium chloride. The process is inexpensive as only sodium chloride is consumed.

A considerable quantity of ferrous iron is frequently present in surface water. This is especially objectionable in the laundry because of the yellow color imparted to the cloth by the oxidation of the iron to the ferric state. The iron is removed by either the lime-carbonate, or the zeolite processes, or by spraying the water to give intimate contact with the air, which oxidizes the iron to insoluble ferric hydroxide.

12. Carbides.—At a very high temperature the metals or their oxides react with carbon forming carbides. The most important is calcium carbide, CaC_2, which is produced on a large scale by heating a mixture of lime and carbon to a temperature of about 3,000° C. in an electric furnace: $CaO + 3C = CaC_2 + CO$. Calcium carbide reacts with water to form acetylene (cf. **XIII—18**): $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$. It may, therefore, be called calcium acetylide. Another important reaction of the carbide is the absorption of nitrogen at about 1,000° C. to form cyanamide: $CaC_2 + N_2 = CaCN_2 + C$. This reaction is the basis for the cyanamide process for the fixation of nitrogen (cf. **XII—8**).

13. Hydrides.—Beryllium and magnesium do not readily form hydrides; but calcium, strontium, and barium react readily with hydrogen at high temperature (about 600°). The large heats of the reactions, e.g. CaH_2, 46 kg. cal., indicate the stable nature of these hydrides. Like the alkali hydrides, the hydrogen possesses a negative valence and is liberated at the anode upon electrolysis of the molten salts. Calcium hydride, although expensive, is an easily portable source of hydrogen for war balloons. One mole reacts with water to give two moles of hydrogen: $CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$.

14. Nitrates.—Calcium nitrate is a constituent of fertile soils. The salt is produced for use as fertilizer by the electric arc process for the fixation of nitrogen (cf. **XII—32**). It crystallizes as $Ca(NO_3)_2 \cdot 4H_2O$ at ordinary temperatures and is very soluble. Strontium nitrate is used in the manufacture of red fire. Barium nitrate is the least soluble of the group, and is precipitated as the anhydrous salt upon the addition of barium ion to solutions containing high concentrations of nitrate. It is sometimes used in making green fire.

15. Sulfides.—The sulfides may be formed by the direct union of the elements, or by reduction of the sulfates by carbon. The compounds so prepared dissolve but slowly in water, but the apparent insolubility is merely a matter of rate of solution. Solutions of these sulfides, like those of all soluble sulfides, are highly alkaline due to hydrolysis of the sulfide ion. Calcium sulfide is used as a depilatory. The use of barium sulfide has been mentioned in the preparation of lithopone. Both of these sulfides glow in the dark after exposure to sunlight, and are used in the preparation of luminous paint. This property is apparently due to the presence of traces of impurities, especially vanadium and bismuth. In the regions about the particles of impurities, the crystal is able to absorb radiant energy through the displacement of electrons to higher energy levels. The rate at which the electrons return to the stabler positions is slow, so that the absorbed energy is re-emitted over a period of time.

16. Phosphates.—The calcium phosphates are the most important of the group. They occur as the tri- and di- calcium orthophosphate, Ca_3PO_4, and $CaHPO_4$; and as fluor and chlor apatites (Par. 4). Dried bones consist largely of calcium phosphate. Millions of tons of the insoluble tricalcium salts

are treated yearly with sulfuric acid to convert into soluble acid phosphate, $Ca(H_2PO_4)_2$, for use as fertilizer (see Superphosphate, **XI—54**). Ammonium magnesium phosphate, $NH_4MgPO_4 \cdot 6H_2O$, is important in analytical work (Par. **18**).

17. Other Important Compounds.—A number of compounds containing the alkaline earths are discussed under other headings: bleaching powder (cf. **X—13**), glass (cf. **XIV—23**), cement (cf. **XIV—24**), asbestos (cf. **XIV—20**), talc (cf. **XIV—21**).

18. Analytical Properties of Alkaline Earth Ions.—The chemistry of the alkaline earth ions is comparatively simple, as they form no complexes with other ions (a few exceptions with beryllium), and few insoluble compounds. The ions are colorless. Beryllium ion has a sweet taste, magnesium ion a bitter taste, and calcium ion is practically tasteless. Barium ion is extremely poisonous. The solubilities of the various hydroxides has been discussed (Par. **7**). The solubilities of the chromate and sulfate decrease with increasing atomic weight; and likewise the carbonate, with the exception that strontium carbonate is more insoluble than barium. The group, not including beryllium, is separated from all other positive ions except the alkalies by taking advantage of the fact that they are not precipitated by a solution of ammonium sulfide. Ammonium carbonate precipitates $CaCO_3$, $SrCO_3$, $BaCO_3$; and if about 30 per cent alcohol is present, $MgCO_3 \cdot (NH_4)_2CO_3$. Radium is separated from barium by fractional crystallization of the chlorides, bromides, or chromates, the compounds of the latter being the more soluble. Barium may be separated from the lighter members of the group by the greater insolubility of the chromate. Strontium is separated from calcium in solution by the addition of a dilute solution of sulfate, which precipitates strontium sulfate but not calcium. Magnesium is separated from the heavier elements of the group through the solubility of the carbonate in ammonium salts. The insoluble nature of beryllium hydroxide permits its ready separation from the remainder of the group. It may be distinguished from aluminum by the solubility of the beryllium hydroxide in excess bicarbonate, probably due to the formation of a complex bicarbonate ion.

Calcium may be precipitated quantitatively as calcium oxalate by the addition of ammonium oxalate. The precipitate is composed of larger crystals, and is more easily filtered if precipi-

tated from a slightly acid solution, in which it is somewhat soluble. The final traces of calcium may then be removed by making the solution alkaline with ammonium hydroxide. The oxalate may be dried and weighed as such or ignited to form the carbonate: $CaC_2O_4 = CaCO_3 + CO$.

Barium is usually precipitated and weighed as sulfate (cf. **XI—33**); while strontium may be determined as sulfate or oxalate. Magnesium ammonium phosphate, $NH_4MgPO_4 \cdot 6H_2O$, is precipitated upon the addition of sodium phosphate and ammonium hydroxide to a solution of a magnesium salt. Upon ignition the pyrophosphate, $Mg_2P_2O_7$, is formed, and may be weighed as such: $2NH_4MgPO_4 \cdot 6H_2O = Mg_2P_2O_7 + 2NH_3 + 13H_2O$.

19. Spectra.—Beryllium and magnesium compounds do not ionize sufficiently to impart color to the Bunsen flame. Volatile calcium compounds give a brick red, strontium a carmine, barium a yellow green, and radium a crimson flame. The coloration is very intense with the chlorides, but is not satisfactory with the oxides or sulfates due to their low volatility. The electric arc spectra afford a much more delicate means of determining the presence of the alkaline earth elements, 0.002 mg. of calcium being detectable. The material to be analyzed is usually placed upon the positive pole of the arc. The wave lengths in $\mu\mu$ (10^{-6} mm.) of the more prominent lines are: calcium 423, 616; strontium 422, 461; barium 455, 493; magnesium 516.8 to 518.4, a group of three lines.

CHAPTER VI

GROUP III. BORON, ALUMINUM

1. The third periodic group, like the first and second groups, is divided into a main group with kernels of the noble gas type, and a subgroup with kernels of the eighteen electron type. The elements of the main group are boron, aluminum, scandium, yttrium, lanthanum (and Rare Earths) and actinium; those of the subgroup are gallium, indium, and thallium. Although the Rare Earths may be considered as members of the third main group, they constitute a family which is so unique from the standpoint of atomic structure that it seems advisable to discuss them in a separate chapter (cf. **XXI**). Due to the great similarity of scandium, yttrium, and lanthanum to the Rare Earths, the detailed consideration of these three elements will be postponed to that chapter. Actinium is of interest chiefly on account of its radioactivity, and will, therefore, be taken up in that connection (cf. **XXII**). The subgroup elements are discussed in Chapter **IX**

Boron is a nonmetal, but the remainder of the group are highly metallic. The melting points of the group are fairly high (Table I), and exhibit no regular trend from the light to the heavy elements. A valence of + 3 is shown by these elements in all of their compounds. The oxides or hydroxides are less basic than those of the alkaline earth elements, as is to be expected from the increased valence of the positive ions. Boron oxide is distinctly acidic and shows only faint basic properties Aluminum oxide is amphoteric, while scandium, yttrium, and lanthanum show no acid properties and are distinctly, though not strongly, basic. This increase in basic character of the oxides within the group is again to be correlated with the increasing size of the ions of the heavier members (cf. **III—7**).

The elements are less electropositive than the alkaline earth metals, though the values for the reaction, $M = M^{+++} + 3E^{-}$, are known only approximately. The energies required to ionize the electrons from the gaseous atoms are very high, as shown for aluminum in Table I; hence the high values for the electrode

potentials of the elements must be due to even greater energies of hydration of the positive ions. In the case of aluminum this is over a thousand kilogram-calories.

TABLE I

Atomic and Physical Properties

	B	Al		B	Al
Atomic weight	10.82	26.97	Ionization potentials in volts, 1st	8.3	5.96
Atomic number	5	13	2d	24.2	18.08
Isotopes	10,11	none	3d	37.8	28.3
Electrons in various quantum levels, 1st	2	2			
2d	3	8	Electrode potential		
3d		3	$M = M^{+++} +$		
Melting points ° C.	2,300	658	$3E^-$, volts 25°		1.69
Boiling points ° C.	2,550	1,800	Electral resistivity		
Density	2	2.70	20° C. ohm-cm.	1.8×10^{6}	2.62×10^{-6}
			Radius of M^{+++} in crystals, cm. $\times 10^{8}$		
			(if $Cl^- = 1.81$)	0.20	0.50

BORON

2. Occurrence.—Boron constitutes but a small portion of the earth's crust, estimated as about 0.001 per cent. It occurs as boric acid, H_3BO_3, and as borates. The principal deposits have resulted from the evaporation of inland seas. In the Stassfurt area in Germany the deposits are chiefly magnesium borates; while in the arid regions of western United States they consist largely of colemanite, $Ca_2B_6O_{11}\cdot 5H_2O$, with some borax, $Na_2B_4O_7\cdot 10H_2O$. Boron is widely distributed in rocks in complex silicates and aluminates, such as tourmaline, $H_2MgNa_9Al_3(BO)_2Si_4O_{20}$.

3. Preparation and Properties.—No satisfactory electrolytic method has been developed for the production of boron. It is usually prepared by the reduction of the oxide by powdered magnesium: $B_2O_3 + 3Mg = 3MgO + 2B$; but other powerful reducing agents, such as sodium, may be used and the halides may be substituted for the oxide. The product of the reduction is amorphous boron, and, when magnesium is used, it is mixed

with magnesium boride, Mg_3B_2, the proportion of which may be minimized by using excess of boric oxide. When the reduction was first carried out with aluminum the product was thought to be crystalline boron, but further investigation has indicated that it consists of a mixture of aluminum borides, such as AlB_{12}.

The free element, as usually prepared, is a dark brown powder. The cooled fused material is brittle, almost as hard as diamond, and practically a non-conductor of electricity.

4. Reactions.—Boron oxidizes slowly in air at 100° C., and burns at higher temperatures with a green flame. It ignites in fluorine at room temperature, and in the other halogens at higher temperatures. It is not oxidized by hydrogen ion, hence it is not a very powerful reducing agent. It does, however, dissolve in fused alkalies due to the stability of the borates. It is readily oxidized by strong oxidizing agents, such as nitric acid, concentrated sulfuric acid, and ferric ion. It does not combine directly with hydrogen. These and other reactions are summarized below.

TABLE II

Reactions of Boron

$2B + 3O_2 = 2B_2O_3$	Burns with green flame
$2B + 3X_2 = 2BX_3$	With halogens
$2B + 3S = B_2S_3$	At about 600°
$2B + N_2 = 2BN$	Above 1,200°
$2B + 2NH_3 = 2BN + 3H_2$	Heated
$2B + 6KOH = 2K_3BO_3 + 3H_2$	Fused with alkali
$B + HNO_3 + H_2O = H_3BO_3 + NO$	
$nB + mM = M_mB_n$	With a large number of metals

5. Oxides.—Boron forms the oxide B_2O_3, and possibly B_2O_2, but the latter is unimportant. The sesquioxide may be prepared by heating boric acid to red heat. The product is a very hard, brittle glass. The oxide dissolves most metal oxides to form clear glasses. The sesquioxide takes up water rather rapidly to form the acid, and since it is otherwise very non-reactive, it often serves as a convenient dehydrating agent.

6. Boric Acid and Borates.—The addition of strong acids to borates liberates the weak boric acid, and this crystallizes from the water solution as the ortho-acid, H_3BO_3. The solubility increases markedly with temperature; a saturated solution contains 2.6 per cent at 0°, and 28.7 per cent at 100° C. The

acid is somewhat volatile from hot solutions, possibly due to the formation of volatile hydrates. Upon heating, the ortho-acid loses water to form first the meta-acid, HBO_2, and then the tetraboric acid, $H_2B_4O_7$. In water solution the ortho-acid acts as a weak monobasic acid. The dissociation constant as calculated for the reaction, $H_3BO_3 = H^+ + H_2BO_3^-$, is 1.7×10^{-9}. The equilibrium is probably complicated, however, by the additional reaction: $2H_2BO_3^- + 2H_3BO_3 = B_4O_7^{--} + 5H_2O$. The acid is used in medicine, under the name "boracic acid," as a mild antiseptic.

Very few ortho-borates are known. Upon the addition of hydroxide to the ortho-acid the equilibrium, $2BO_2^- + 2HBO_2 = H_2O + B_4O_7^{--}$, appears to be established. Many of the meta borates are but moderately soluble, e.g. $AgBO_2$, $Ba(BO_2)_2$, $Pb(BO_2)_2$. With sodium hydroxide the salt, $Na_2B_4O_7 \cdot 10H_2O$, **borax,** forms, and may be crystallized from the solution below 60° C. Above that temperature a pentahydrate is stable.

Borax is the most important compound of the element. It is but sparingly soluble at 0° C., 1.3 g. per liter, but is very soluble at the temperature of transition to the pentahydrate. The solution is slightly alkaline by hydrolysis, $0.1N$ solution containing about $5 \times 10^{-4}N$ OH^-. Borax is prepared from naturally occurring borates by (1) the extraction of the acid, and (2) the reaction of the acid with sodium carbonate: $4H_3BO_3 + Na_2CO_3 = Na_2B_4O_7 + 6H_2O + CO_2$.

Borax fuses to form a glass which is capable of dissolving metal oxides, since it contains an excess of acid oxide, e.g. $Na_2O \cdot 2B_2O_3 + CuO = Na_2O \cdot B_2O_3 + CuO \cdot B_2O_3$. Upon this property depends its use in soldering and welding to clean the metal surface of coatings of oxides. Many oxides dissolved in fused borax impart characteristic colors, the familiar borax bead tests (Append. VII). The colored glass finds use as artificial gems, and when ground, as pigments. Among other important uses of borax are the manufacture of glass, enamels, and soap, sizing for paper, and as a preservative for wood and meats.

Beside the borates above mentioned there exist a very large number of polyborates, salts of the acids, $(B_2O_3)_n(H_2O)_m$, where n may be as large as six and m is usually one, two, or three.

7. Boric acid forms with methyl alcohol the rather volatile methyl borate, $(CH_3)_3BO_3$. This compound burns with a green

flame. The corresponding ethyl borate is less volatile. The very slightly basic nature of boric acid is shown by the reaction between boiling boric acid and phosphoric acid to give **boron phosphate,** $H_3BO_3 + H_3PO_4 = BPO_4 + 3H_2O$. Borax fused with ammonium chloride forms boron nitride: $Na_2B_4O_7 + 4NH_4Cl = 4BN + 2NaCl + 7H_2O + 2HCl$. **Boryl sulfate,** $(BO_2)_2SO_4$, is formed by the action of sulfur trioxide upon boron trichloride.

8. Peroxyborates.—Peroxyborates may be prepared by the action of peroxides upon borates or by the electrolytic oxidation of borate solutions. The most important of these compounds is the sodium salt, $NaBO_3 \cdot 4H_2O$. It is used as a bleaching agent, and as an antiseptic constituent of certain tooth powders.

9. Borides.—In addition to the borides of magnesium and aluminum mentioned above, a large number of borides have been prepared, among which the following may be mentioned: AlB_2, CaB_6, BaB_6, CB_6, SiB_6, ThB_4, CrB, WB_2, FeB, Fe_2B, NiB, CoB.

10. Halides.—The halides are gases, or easily volatile liquids. The melting and boiling points parallel the corresponding values for the halogens.

	BF_3	BCl_3	BBr_3	BI_3
Boiling point	− 101	13	90.5	210
Melting point	− 127	− 107	− 44	43

They may be prepared by the direct union of the elements, but are usually formed from boric oxide, using hydrogen fluoride in the case of fluorine, $B_2O_3 + 6HF = 2BF_3 + 3H_2O$; and in the case of the other halogens using the halogen and carbon at elevated temperatures: $B_2O_3 + 3C + 3X_2 = 2BX_3 + 3CO$. The three heavier halides are completely hydrolyzed in water: $BX_3 + 3H_2O = H_3BO_3 + 3H^+ + 3X^-$. The fluoride reacts with water to form boric acid and fluoboric acid: $4BF_3 + 3H_2O = H_3BO_3 + 3HBF_4$. Pure fluoboric acid is unstable, but many of its salts are known. Boron fluoride also forms a complex with ammonia, BNH_3F_3. The probable electronic formulae of the fluoride, the ammonia complex, and fluoboric acid are, respectively:

11. Hydroborons.—There are a number of compounds of hydrogen and boron which resemble the hydrocarbons in their non-polar nature. They are often referred to as the boron hydrides, but it seems advisable to restrict the use of the term "hydrides" to compounds in which the hydrogen is definitely negative. The addition of magnesium boride to 4*N* HCl at about 45° results in the evolution of a gas which is mainly hydrogen, but contains as well the compound, B_4H_{10}, borobutane, and small amounts of B_5H_9, B_6H_{10}, and B_6H_{12}. Borobutane boils at 10° and melts at − 112°. It has a disagreeable odor, is toxic, and ignites spontaneously when exposed to air. The gas is unstable in respect to decomposition into B_2H_6 and a number of complex solids and liquids. The compound, BH_3, does not appear to be stable, possibly due to polymerization. The structure of these compounds is difficult to explain, as there do not appear to be enough electrons in B_4H_{10}, for example, to account for all the necessary bonds.

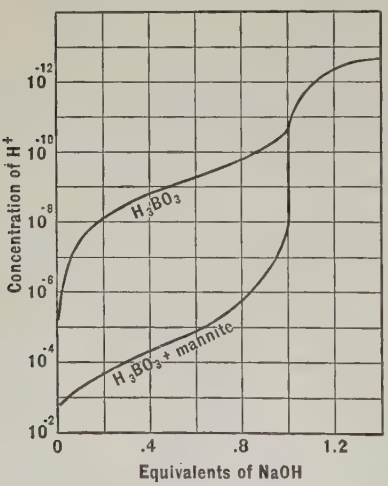


FIG. 1.—Titration curves for boric acid.

12. Analytical.—The green flame test of methyl borate is often employed as a qualitative test. The sample is placed in a test tube, and sulfuric acid and methyl alcohol added. The vapors which escape upon gentle warming burn with a green flame when ignited.

Methyl orange does not react acid to boric acid, therefore soluble borates may be titrated with that indicator. Pure boric acid is difficult to titrate with a strong base, as the equivalent point is highly alkaline as indicated in Figure 1. The addition of glycerol or mannite to the

solution has the remarkable effect of increasing markedly the strength of the acid, and bringing the equivalent point into the range of phenolphthalein; hence the acid may be titrated using that indicator.

ALUMINUM

13. Occurrence.—Aluminum ranks third among the elements in order of abundance expressed as per cent by weight of the earth's crust, ocean, and atmosphere, the value being about 7 per cent. It is the most abundant of the metallic elements. The most common minerals are the aluminosilicates, which include the feldspars, as $KAlSi_3O_8$; the micas, as $H_2KAl_3(SiO_4)_3$; and clays (kaolin), as $H_2Al_2(SiO_4)_2H_2O$. Cryolite, Na_3AlF_6, and bauxite, $Al_2O_3 \cdot 2H_2O$, are important as sources of the metal. Ruby, sapphire, and corundum are forms of the oxide. Garnet is, approximately, [Ca, Mg, Fe][Al, Fe]$_2(SiO_4)_3$; and turquoise, $Al_2(OH)_3PO_4 \cdot H_2O$, colored by copper phosphate.

14. Preparation.—The metal was first prepared commercially about 1850 by the reduction of the chloride by sodium at high temperature. Shortly thereafter methods were developed for the electrolysis of mixtures of molten aluminum, sodium fluorides, and chlorides, but the metal remained rare and expensive until the simultaneous discovery by Hall and by Héroult of the electrolysis of the oxide in molten cryolite in 1886, which laid the foundation of the modern aluminum industry. In the Hall process, the electrolysis is carried out in large iron pots with a thick carbon lining which acts as the cathode. A number of large graphite rods sticking down into the pot serve as the anode. The graphite rods are first lowered until they touch the cathode and an arc is struck; powdered cryolite is then added and melted by the heat of the arc. When a sufficient liquid bath is obtained, aluminum oxide is added and the anodes drawn farther away from the cathode. The addition of the oxide lowers markedly the resistance of the liquid. The temperature of the bath is kept at about 1,000° C., and since this is above the melting point of the metal, it collects as a liquid in the bottom of the cell and is drawn off at intervals. Oxygen is liberated at the anode and gradually burns away the graphite. The cell reaction is: $2Al_2O_3 = 4Al + 3O_2$. Ordinary commercial aluminum is about 99.0 to 99.5 per cent pure. It has not been possible

to refine the impure metal, so the oxide is carefully purified before electrolysis (see Oxide). Recently, however, aluminum of 99.85 per cent purity has been made electrolytically from an alloy of aluminum, copper and silicon. The cell consists of three liquid layers of decreasing density; the lowest is the alloy, which is made the anode; the middle layer consists of molten salts; and the top layer is pure aluminum, which is made the cathode.

15. Properties.—The metal is extremely light, density 2.6, and possesses high tensile strength. Although its specific electrical conductivity is less than copper, weight for weight it is twice as good a conductor. It is easily malleable and may be rolled into thin foil. It has a silvery appearance when freshly cut, but the ordinary surface has a dull white luster, since it is covered by a thin, firm coat of oxide which protects the surface from further oxidation.

16. Uses.—In addition to the common use in household utensils, the metal is becoming increasingly important in the construction of airplanes and other machines where light weight is essential. Two of its largest uses are as foil in place of tin foil, and as a "silver" paint. The latter is made by mixing the finely ground metal with oil. Aluminum wire to the extent of 150,000 miles was in use in 1926, chiefly in transmission lines. The metal is used to remove dissolved oxygen in casting iron and steel, and thus to prevent blow holes. It is also used in "thermite" (Par. 17). The metal can be welded, but it is soldered with difficulty. Many of the alloys are extremely important. The pure metal is difficult to work on a lathe because it sticks to the tools, but the alloy with 2 per cent magnesium called "**magnalium**" may be machined readily. "**Duralumin**" contains 4 per cent copper, 0.5 per cent magnesium, and 0.6 per cent manganese; and when hardened by quenching, possesses a tensile strength of 60,000 lbs. per sq. in., as compared to 30,000 lbs. for the pure metal.

17. Reactions.—Aluminum is a very base metal, but its surface is protected so thoroughly by its oxide coating that it may be melted in air without serious oxidation. However, at high temperatures the metal burns vigorously, and aluminum powder and liquid oxygen unite with a flash if ignited with a match. The metal does not dissolve in water unless the surface is amalga-

mated. The oxide does not adhere to the amalgamated surface, and the metal is free to show its true electropositive nature by reacting with water or by oxidizing rapidly in air. The metal dissolves readily in hydrochloric acid, and slowly in sulfuric acid, but is rendered passive by nitric acid so that this acid is often shipped in aluminum containers. It dissolves rapidly in nitric acid, however, if a small amount of mercuric salt is present. Nitric oxide is evolved from concentrated acid, and ammonium nitrate formed with dilute. Concentrated alkalies dissolve the metal with the evolution of hydrogen and the formation of the aluminate. The granulated metal reduces many oxides and sulfides upon ignition, the so-called "**Goldschmidt reaction.**" A mixture of aluminum and iron oxide, known as "**thermite,**" is used in welding. The heat of the reaction is such that a temperature of about 3,000° is produced, and the iron formed by the reduction can be run as a white hot liquid into the crack to be welded. To start the thermite reaction an ignition powder is required, such as a mixture of barium peroxide and aluminum.

The aluminum electrode is highly irreversible, and extremely difficult to measure directly. The value, 1.69 volts, is calculated from thermal data and indicates that aluminum is about as electropositive as magnesium.

The irreversibility of the aluminum electrode is made use of in rectifying alternating currents. When acting as anode, the electrode has enormous resistance, but as cathode it has low resistance; hence cells with an aluminum electrode allow one half of an alternating current to pass but not the other. The cell is most effective with a phosphate electrolyte.

TABLE III

REACTIONS OF ALUMINUM

$2Al + 3O_2 = Al_2O_3$	
$2Al + 6H^+ = 2Al^{+++} + 3H_2$	
$2Al + 2OH^- + 4H_2O = 2H_2AlO_3^- + 3H_2$	
$Al(amalgam) + 6H_2O = 2Al(OH)_3 + 3H_2$	
$Al(amalgam) + 4H^+ + NO_3^- = Al^{+++} + NO + 2H_2O$	Dilute nitric forms NH_4^+
$2Al + Fe_2O_3 = Al_2O_3 + 2Fe$	Analogous reaction with many oxides and sulfides
$2Al + 3X_2 = 2AlX_3$	With halogens
$2Al + 6S = 2Al_2S_3$	At high temperature
$2Al + N_2 = 2AlN$	Slowly at high temperature
$6Al + 3CO = Al_4C_3 + Al_2O_3$	At high temperature.

18. Oxide and Hydroxide.—The oxide occurs in nature as corundum. When colored red it is called ruby, and when blue, sapphire. The color in the former is due to a trace of chromium, while that of the latter is attributed to iron and titanium. When it contains magnetite, it is known as emery. Artificial corundum, made by fusing the precipitated hydroxide in an electric furnace, is sold under the name "alundum," and artificial rubies and sapphires are now produced in large quantities. Corundum stands next to diamond and carborundum in hardness, and is used as an abrasive, and also in making refractory crucibles. The oxide is formed upon heating the hydroxide. Unless it has been ignited strongly, it will reabsorb water to form the hydroxide, and hence may be employed as a drying agent.

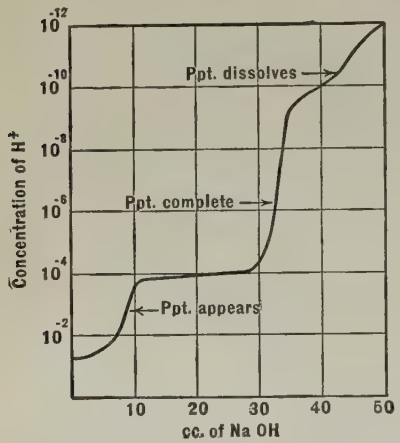


FIG. 2.—Precipitation and solution of aluminum hydroxide in alkali.

Aluminum hydroxide precipitates as $Al(OH)_3$, i.e. $Al_2O_3 \cdot 3H_2O$. Upon heating it loses water to form $HAlO_2$, i.e. $(Al_2O_3 \cdot H_2O)$. Both of these compounds together with bauxite, $Al_2O(OH)_4$, i.e. $(Al_2O_3 \cdot 2H_2O)$, are found in nature. Aluminum hydroxide is insoluble in water and is amphoteric, dissolving in both acids and bases: $Al(OH)_3 + 3H^+ = Al^{+++} + 3H_2O$ and $Al(OH)_3 + OH^- = H_2AlO_3^- + H_2O$. The hydroxide is dissolved but slightly by ammonium hydroxide, especially in the presence of ammonium salt, to repress the concentration of hydroxide ion. The concentrations of hydroxide and hydrogen ions involved in the precipitation and solution of the hydroxide are indicated in Figure 2. Soluble carbonates, sulfides, acetates, cyanides, and other salts of weak acids precipitate aluminum hydroxide by complete hydrolysis of both ions.

The pure oxide required for the electrolytic preparation of the metal is made from bauxite or other hydrated oxides. The mineral is first dissolved in sodium hydroxide to form a solution

of sodium aluminate; and the hydroxide is then reprecipitated by passing in carbon dioxide, or by allowing the solution to stand in contact with crystallized $Al(OH)_3$. In the latter case, the crystallized and insoluble form slowly precipitates (see Beryllium Hydroxide). Many attempts have been made to prepare the pure oxide from clay, but no commercial process has yet been developed.

19. Aluminates.—Sodium and potassium aluminates are soluble but highly hydrolyzed. Most of the aluminates are, however, insoluble. The meta aluminates of the divalent metals, $M(AlO_2)_2$, occur as a mineral type known as spinels. Many complex aluminates exist, but few as simple ortho salts. The addition of ammonium hydroxide to a solution of aluminum and zinc salts precipitates aluminum hydroxide with some zinc aluminate. The formation of blue cobalt aluminate is mentioned under the analytical properties of aluminum. Calcium aluminate is an essential constituent of Portland cement (cf. **XIV—24**).

20. Halides.—The anhydrous halides may be prepared by the direct action of the halogen upon the metal, while solutions of the halides are formed by the action of the halogen acids upon the metal or hydroxids. Upon evaporation of the solutions, the halides may be obtained as highly hydrated compounds, e.g. $AlCl_3 \cdot 6H_2O$. When heated, the hydrates hydrolyze completely to the oxide and the halogen acid, which is evolved. The anhydrous chloride is employed as a catalytic agent in many organic reactions. Its sublimes without melting at ordinary pressures, the sublimation temperature being 183° at 760 mm.

The halides form compounds with ammonia similar in nature to the hydrates, thus $AlCl_3 \cdot 6NH_3$ forms at ordinary temperatures by the action of ammonia gas upon the salt. Aluminum fluoride exhibits strong tendencies to form complex salts, giving the radical, AlF_6^{---}, as in cryolite, Na_3AlF_6. These compounds are analogous to the aluminate, and owe their stability to the large value of $ee'/(r + r')$ (cf. **III—7**) for aluminum and fluoride ions. The tendency of the other halides of aluminum to form complexes decreases with increasing weight.

21. Sulfates.—The sulfate, $Al_2(SO_4)_3 18H_2O$, may be crystallized with difficulty from solutions at ordinary temperatures. It is highly soluble, and gives a very acid solution by hydrolysis. A $0.25M$ solution is about 0.5 per cent hydrolyzed, assuming

that the hydrolysis reaction is $Al^{+++} + H_2O = Al(OH)^{++} + H^+$. The sulfate is prepared from either bauxite or clay by treating with sulfuric acid. The latter reaction is: $H_2Al_2(SiO_4)_2 \cdot H_2O + 3H_2SO_4 = Al_2(SO_4)_3 + 2H_2SiO_4 + H_2O$. The silicic acid is insoluble, and may be filtered off.

With the alkali sulfates, except lithium, and with ammonium, silver, and thallous sulfates, aluminum sulfate forms isomorphous compounds of the general type, $MAl(SO_4)_2 12H_2O$, known as **alums.** The class is even more general, and the aluminum may be substituted by Fe^{+++}, Cr^{+++}, Mn^{+++}, Ti^{+++}, and other trivalent ions. The tendency of the alkali elements to form alums increases with increasing atomic weight; cesium forms more alums than the others and these are in general less soluble. The ammonium and potassium alums are the most important commercially. These alums are very soluble in hot water, but much less in cold, so that they may readily be purified by crystallization.

The principal uses of aluminum sulfate and alum depend primarily upon the hydrolysis of the aluminum ion, and may be divided into two classes: (1) those depending upon properties of hydrogen ion, and (2) those depending upon the properties of aluminum hydroxide. In the first class may be mentioned the use in baking powder to furnish acid to cause the liberation of carbon dioxide. The same reaction is employed in certain fire extinguishers, in which solutions of alum are caused to react with solutions of sodium bicarbonate containing organic substances capable of forming very stable foams. To the second class belong the uses as a mordant in dyeing, and as a clarifying agent for water. Aluminum hydroxide, formed by the addition of sodium carbonate or lime to alum or aluminum sulfate, is a very good absorbent for certain dyes, and also attaches itself to the fiber, thus serving to bind the dye to the material. (cf. Hildebrand, *Princ. of Chem.*, p. 333). **Mordants** of this nature are frequently necessary in dyeing cotton goods. Certain dyes may also be adsorbed on aluminum hydroxide to form pigments known as "**lakes.**" The action of alum in water clarification is again due to the adsorption of suspended material by the gelatinous precipitate. Alum is also used in sizing paper and in fireproofing fabric. When heated it loses water and some sulfur trioxide; the product, known as "burnt alum," is used in medicine as an "astringent."

22. Ultramarine.—A complex sodium aluminum silicate and sulfide occurs in nature as the mineral lapis lazuli. When ground, it constitutes the blue pigment, ultramarine. The pigment is now manufactured by heating a mixture of clay, sodium sulfate, and carbon, and is much used for laundry blue, as a water color, and in neutralizing yellow tones in linen, starch, paper, and granulated sugar. It is stable toward alkalies, but evolves hydrogen sulfide with acids.

23. Other Compounds of Aluminum.—**Aluminum sulfide,** Al_2S_3, is formed by the reduction of metallic sulfides by aluminum at high temperatures. It is completely hydrolyzed in water. **Aluminum acetate,** $Al(C_2H_3O_2)_3$, has many uses similar to those of the sulfate. It may be prepared from the sulfate by metathesis with barium acetate. **Kaolin,** the hydrated silicate, is further discussed under silicon.

24. Analytical Properties of Aluminum Ion.—Aluminum ion is colorless, and has a slightly bitter astringent taste. It forms an insoluble amphoteric hydroxide as already discussed. The ortho-phosphate, $AlPO_4$, is insoluble, and precipitates upon the addition of a soluble phosphate and ammonium hydroxide to aluminum ion. The separation of aluminum from other positive ions, and its identification as the hydroxide, is outlined in the general scheme of analysis (Append. VI). Precipitated aluminum hydroxide is often confirmed by moistening the precipitate with a few drops of cobalt nitrate solution and igniting at red heat. A blue residue (cobalt aluminate) indicates the presence of aluminum. The test is capable of detecting 0.2 mg. of aluminum. It is necessary in carrying out the test to have the aluminum oxide in excess, as otherwise the color observed is obscured by the black cobalt oxide. The test is not satisfactory if sodium or potassium salts are occluded in the precipitate in any large amounts.

Complex aluminates may be got into solution by fusion in a platinum dish with potassium acid sulfate or with sodium carbonate, followed by extraction with hydrochloric acid. Silica is removed by evaporating to dryness, boiling again with hydrochloric acid, and filtering.

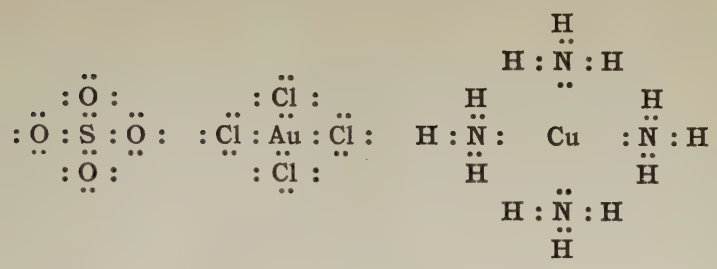
Aluminum is generally determined in quantitative analysis by precipitating as the hydroxide and weighing as the oxide.

CHAPTER VII

SUBGROUP I. COPPER, SILVER, AND GOLD

1. The elements of Subgroup I, copper, Cu (cuprum), silver, Ag (argentum), and gold, Au (aurum), differ markedly in properties from the elements of the main group. Unlike the alkalies they are "noble" metals and are not readily oxidized. This property may be correlated (cf. III—5) with the higher boiling points of the metals, indicating greater difficulty in separating their atoms from each other, and with the larger ionization potentials of the gaseous atoms (Table I). Their oxides, of the type M_2O, are much less basic than the alkali oxides, a fact which is related to the smaller size of the ions (cf. Table I, also III—7). These elements also form certain compounds in which they have valences greater than $+1$; in fact, the ions of divalent copper and trivalent gold are in general more stable in respect to reducing agents than the monovalent ions. The outer electron shell of the kernel is not of the noble gas type, but contains 18 electrons, and these higher valence states exist through the possibility of removing one or two electrons from this shell. This process is impossible in the case of the main group elements, since the energies of their kernel electrons are very much greater.

2. The ions of the subgroup elements possess the property of forming very stable complexes, such as $Cu(NH_3)_4^{++}$, $Ag(CN)_2^-$, $AuCl_4^-$. This property is in general strongly exhibited by all ions with more than eight electrons in the outer shell of the kernel, and appears to arise from a very powerful positive field at a short distance from the ion. These complexes have been called **coordination compounds,** and the number of groups or ions held by the positive ion is termed its **coordination number.** They probably differ only in degree from the very stable oxygen complexes of the acid oxides, as indicated by the electronic formulæ:



Sulfate ion Chloraurate ion Cupric ammonia ion

However, a number of anomalies are shown in the formation of these complexes. Thus fluoride ion, which exhibits strong tendencies to form complexes with the smaller ions such as aluminum, does not readily form complexes with the subgroup elements. The stability of the complexes and also the solubility of the compounds of the ions appear to be related to the electrical distortion or polarization of the negative ions. This relation is illustrated by the following comparison of the solubilities of a number of silver salts with the indices of refraction of the negative ions, which may be taken as a measure of the polarization.

	F^-	O^{--}	Cl^-	Br^-	I^-	S^{--}
Solubility of silver salt moles/liter	13.5	2×10^{-4}	9×10^{-6}	6×10^{-7}	1×10^{-8}	$<10^{-8}$
Index of refraction of negative ion per g. atom	2.5	7.0	9.0	12.7	19.2	20.0

Moreover, in the more stable compounds, the values for the ionic radii are considerably less than those given in Table I, indicating that distortion of the negative ion occurs in these compounds.

3. The basic nature of the oxide (comparing the univalent oxides) increases with increasing size of the atom, but the electropositive nature of the metal, i.e. ease of oxidation, decreases; gold being one of the most noble metals. The metals are all excellent electrical conductors.

COPPER

4. Occurrence.—Copper frequently occurs in the free state. As a rule such deposits are small, but in the Lake Superior

region masses of native copper have been found weighing many tons. The copper ores may be classified as: (1) sulfides ores, the more important being chalcopyrite, $CuFeS_2$, bornite, approximately Cu_3FeS_3, chalcocite, Cu_2S, and indigo copper, CuS; (2) oxidized ores, consisting of the oxides and their compounds with negative elements, such as cuprite, Cu_2O, melaconite, CuO, malachite, $Cu_2(OH)_2CO_3$, azurite, $Cu_3(OH)_2(CO_3)_2$, chrysocolla, $CuSiO_3 \cdot 2H_2O$, and atacamite, $CuCl_2 \cdot 3CuO \cdot 3H_2O$.

TABLE I

ATOMIC AND PHYSICAL PROPERTIES

Element	Copper	Silver	Gold
Symbol	Cu	Ag	Au
Atomic number	29	47	79
Atomic weight	63.57	107.880	197.2
Isotopes	63,65	107,109	undetermined
Number of electrons in various quantum levels, 1st	2	2	2
2d	8	8	8
3d	18(17)	18	18
4th	1(2)	18	32
5th	—	1	18(16)
6th	—	—	1(3)
Color of metal	red	silver	yellow
Density	8.94	10.5	19.3
Melting point, ° C.	1,083	960	1,063
Boiling point, ° C.	2,300	1,950	2,600
Tensile strength, lbs./sq. in.	60,000	42,000	20,000
Specific resistance at 20°, ohm/cm. $\times 10^6$	1.72	1.59	2.44
Ionization potential of gaseous atom, volts	7.69	7.54	8.
Radius of M^+ in solids, $\times 10^8$ cm. (if $Cl^- = 1.81$)	0.96	1.26	1.37
Potential of electrode, $M = M^+(aq) + E^-$ (hydrogen electrode = 0)	−0.51	−0.799	−1.5

5. Metallurgy.—The methods employed in winning copper from its ores vary greatly with the type of ore. With native copper the rock is crushed, the copper concentrated by mechanical methods, and the metal purified by melting with a flux to remove the remaining gangue. High grade oxidized ores are smelted by heating in a furnace with a mixture of coke and suitable fluxes. Low grade ores may be worked by extraction of the

copper with ammonia or other solvents. About 70 per cent of the copper in the United States is produced from sulfide ores. The procedure is somewhat complicated because the sulfide is not readily reduced, and also because of the difficulty in removing the large amount of iron which is always present. The steps in the process are: (1) concentration of the ore (only with low grade ores), (2) roasting, (3) formation of "copper matte," largely Cu_2S and FeS, (4) reduction of the matte to "blister copper," (5) refining of the "blister copper."

The concentration of low grade ores is now usually carried out by the "flotation" methods. The ore is ground with oil and water. The sulfide particles are wet by the oil and the earthy particles by the water. The mass is added to a larger amount of water containing a foaming agent and beaten or blown into a foam. The sulfide particles collect at the surface of the bubbles and are carried off with the foam, while the earthy particles, or "gangue," settle to the bottom. It is claimed that the method will remove as much as 95 per cent of the metal from an ore containing as low as 2 per cent copper.

The roasting step serves to remove volatile oxides of arsenic and antimony, and to oxidize part of the sulfides to the metallic oxides and sulfur dioxide. The next step is the formation of the copper matte by heating the ore with addition of sand or calcium carbonate in the proper proportion to form easily fusible calcium silicate slag. This is carried out either in a reverberatory furnace in which hot flames of burning coal dust are played upon the surface of the charge, or in a blast furnace where a blast of air is blown through the charge. In the latter case coke is added to the mixture, and its combustion supplies the heat. The temperature is kept high enough to melt the charge, and the heavier mixture of the molten sulfides settles beneath the lighter slag. During the process some of the iron is removed as iron silicate, and some of the sulfur is oxidized to sulfur dioxide. The matte consists of cuprous and ferrous sulfides. The next step is now generally carried out in the so-called copper converter, a barrel shaped vessel provided with a number of blast pipes. Air is blown through the charge, to which sand has been added, and the ferrous sulfide is converted to ferrous oxide, which forms ferrous silicate: $2FeS + 3O_2 = 2FeO + 2SO_2$, and $FeO + SiO_2 = FeSiO_3$. When the iron sulfide is all oxi-

dized, the blast is stopped and the slag poured off. The blast is then renewed and metallic copper formed by the oxidation of the sulfur: $Cu_2S + O_2 = 2Cu + SO_2$. The copper is poured into molds, and upon cooling evolves some dissolved sulfur dioxide, which gives the surface a "blistered" appearance.

About 70 per cent of the blister copper in the United States is refined by the electrolytic method, wherein the crude metal is made the anode in a cell containing an acid solution of copper sulfate. A thin plate of pure copper serves as the cathode. By regulating the potential drop across the cell, it is possible to dissolve copper and the baser metals at the anode, leaving behind the more noble metals, such as silver, gold, and platinum as an "anode sludge." The difference in the electro-potential of copper and the base metals, iron, zinc, lead, and nickel, is sufficient so that in the acid solution copper is preferentially deposited at the cathode with a purity of approximately 99.9 per cent.

In the older methods of refining blister copper, the metal is heated in a silica lined vessel, with agitation to bring about oxidation of the base metals by the air. The basic oxides then form a slag with the silica lining. The principal impurity now present is cuprous oxide which is soluble in molten copper; so after skimming off the slag, the metal is stirred with a pole of green wood, and the hot hydrocarbons liberated from the wood reduce the cuprous oxide. The process does not give as pure copper as the electrolytic method, nor does it render possible the recovery of the more noble metals.

6. The Metal.—The more important physical properties are given in Table I. The yearly production of copper is about a million tons, of which the United States produces about 60 per cent. Its principal use, due to its high electrical conductivity and good ductility, is in electrical transmission. For this purpose it must be extremely pure, since the presence of a few tenths of a per cent of certain impurities, especially arsenic, greatly increases the resistance. Because of its high thermal conductivity and comparative inertness, it is used in boilers, water heaters, cooking utensils, steam pipes, etc. It is used in the electrotyping processes now generally employed in reproducing engravings and printing books. A plaster or wax cast is made of each page of type, the cast is coated with graphite to

render it conducting, and copper is then deposited upon the cast electrolytically. The deposit of copper is then removed and strengthened by filling the back with lead.

A summary of the composition of the more important alloys of copper is given in Table II. Bronze is much harder than copper, and also more readily cast into molds. Aluminum bronze resembles gold in color, and is used in gilt paint. Brass foil is often used as a substitute for gold leaf. German silver, as its name indicates, resembles silver in appearance. It is a very poor conductor of heat. Phosphor bronze is employed in bearings. Constantan has a high and very reproducible thermoelectric force against copper, and the copper-constantan thermocouple is used in the measurement of temperature.

TABLE II

Copper Alloys

Brass	60–90 Cu, 10–40 Zn
Bronze	80 Cu, 15 Sn, 5 Zn
Aluminum bronze	90 Cu, 10 Al
Phosphor bronze	80 Cu, 10 Sn, 9 Sb, 1 P
Manganese bronze	70–95 Cu, 5–30 Mn
Silicon bronze	95 Cu, 5 Si
Gunmetal	90 Cu, 10 Sn
Bell metal	78 Cu, 22 Sn
Constantan	60 Cu, 40 Ni
Manganin	82 Cu, 15 Mn, 3 Ni
German silver	52–60 Cu, 25 Zn, 15–22 Ni

TABLE III

Reactions of the Metal

$2Cu + O_2 = 2CuO$	Rapid at about 300°
$4Cu + O_2 = 2Cu_2O$	At about 1,000°
$Cu + F_2 = CuF_2$	Also with Cl_2 and Br_2. I_2 forms CuI.
$2Cu + S = Cu_2S$	Upon heating. Also with Se, Te, P
$Cu + 2H^+ + \frac{1}{2}O_2 = Cu^{++} + H_2O$	With any acid not too weak
$Cu + 4NH_3 + \frac{1}{2}O_2 + H_2O = Cu(NH_3)_4(OH)_2$	
$2Cu + O_2 + CO_2 + H_2O = Cu_2CO_3(OH)_2$	Corrosion in air
$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$	Hot conc. acid
$Cu = Cu^{++} + 2E^-$	In general with oxidizing agents of potential greater than -0.34 volts, e.g. HNO_3

7. Valence States and Oxidation and Reduction.—Copper forms compounds of valence numbers, + 1 (cuprous), + 2

(cupric), and a few unstable compounds of + 3. Important potential values dealing with the oxidation and reduction of cuprous and cupric compounds have been summarized in Table IV.

TABLE IV

OXIDATION REDUCTION POTENTIALS OF COPPER

	Volts$_{25°}$
$Cu + HS^- + OH^- = CuS + H_2O + 2E^-$	+ 0.89
$2Cu + 2OH^- = Cu_2O + H_2O + 2E^-$	+ 0.35
$Cu + 2OH^- = Cu(OH)_2 + 2E^-$	+ 0.21
$Cu + I^- = CuI + E^-$	+ 0.17
$Cu_2O + 2OH^- + H_2O = 2Cu(OH)_2 + 2E^-$	+ 0.08
$Cu + Br^- = CuBr + E^-$	− 0.05
$Cu + Cl^- = CuCl + E^-$	− 0.13
$Cu^+ = Cu^{++} + E^-$	− 0.18
$Cu = Cu^{++} + 2E^-$	− 0.34
$Cu = Cu^+ + E^-$	− 0.52
$CuCl = Cu^{++} + Cl^- + E^-$	− 0.55
$CuI = Cu^{++} + I^- + E^-$	− 0.85

In the case of soluble salts giving the ions Cu^+ and Cu^{++}, it is easier to oxidize the metal to the cupric state than to the cuprous, and this also means that the equilibrium, $2Cu^+ = Cu + Cu^{++}$, favors the reactions as written: e.g. cuprous nitrate will decompose into cupric nitrate and copper. Also the reduction of cupric ion in such solutions will yield the metal and not cuprous ion.

However, cuprous ion forms many very slightly soluble salts and very stable complex ions, and with many of these the above equilibria are reversed. The following are a number of important examples:

(*a*) *Halides.* Cupric chloride and bromide are reduced, e.g. by electrolysis or by the metal, to the cuprous salt. The addition of iodide to cupric ion results in the liberation of iodine: $Cu^{++} + 2I^- = CuI + \frac{1}{2}I_2$.

(*b*) *Cyanide.* Cupric ion and cyanide give cuprous cyanide ion and cyanogen (or cyanate in ammonia solutions): $2Cu^{++} + 8CN^- = 2Cu(CN)_3^{--} + C_2N_2$. This complex is so stable that the metal will dissolve in hydrogen cyanide, in spite of its weakness, with the evolution of hydrogen: $Cu + 3HCN = H_2Cu(CN)_3 + \frac{1}{2}H_2$.

(*c*) *Oxide.* The reduction of cupric compounds in alkaline

solution gives cuprous oxide, Cu_2O. This is the basis for the common test for sugar (specifically dextrose). An alkaline solution of copper sulfate and Rochelle salts, $NaKC_4H_4O_6 \cdot 4H_2O$, known as **Fehling's solution**, will give a red coloration with extremely small quantities of dextrose, due to the precpitiation of Cu_2O.

(*d*) *Reduction upon Heating.* Cupric compounds are in general unstable in respect to the cuprous upon heating. $2CuO = Cu_2O + \frac{1}{2}O_2$. The partial pressure of oxygen becomes appreciable above 900° C. However, the two oxides appear to form a solid solution in each other so that the partial pressure depends both upon the temperature and the concentration of the two oxides. Cupric sulfide decomposes at red heat: $2CuS = 2Cu_2S + S$. The cupric halides decompose according to the equation: $2CuX_2 = CuX + 3/2X_2$. Cupric fluoride decomposes around 500°, and the chloride and bromide at somewhat lower temperatures. The iodide is not stable even at room temperatures.

7. Powerful oxidizing agents, especially in alkaline solution, oxidize copper to the trivalent oxide, Cu_2O_3. This compound is very unstable; it tends to evolve oxygen and it reacts readily with reducing agents. It appears to be of a distinctly acidic nature.

8. Cuprous Ion and Cuprous Compounds.—Cuprous compounds are prepared from the cupric by methods based upon the reactions discussed in the preceding paragraph. The ion, and in general its complex ions, are colorless. The **oxide** occurs in nature. It has a fine red color, and for that reason is employed in making ruby glass and in coloring porcelain. For the arrangement of the ions in the crystal lattice see Appendix V. It is insoluble in water and alkalies. The precipitated oxide is hydrated, but a base of the definite composition CuOH does not appear to exist. It reacts with sulfuric, nitric, and hydrofluoric acids to give copper and the cupric salt. It dissolves in ammonia, alkali cyanide, and hydrochloric acid to form the complex ions: $Cu(NH_3)_2^+$, $Cu(CN)_3^{---}$ and $CuCl_2^-$. The cuprous chloride and ammonia solution is oxidized by oxygen to the cupric compound, and advantage is sometimes taken of this in removing oxygen from gas: $2Cu(NH_3)_2^+ + 2NH_4OH + \frac{1}{2}O_2 = 2Cu(NH_3)_4^{++} + 2OH^- + H_2O$. The **chloride, bromide,** and **iodide** are slightly soluble in water, the solubility decreasing in

the order given, as with the corresponding silver halides. They are all soluble in excess of the halide ion: e.g. $CuBr + Br^- = CuBr_2^-$. The chloride is hydrolyzed in boiling water: $2CuCl + H_2O = Cu_2O + 2H^+ + 2Cl^-$. A solution of chlorcuprous acid, $HCuCl_2$, is employed in gas analysis to absorb carbon monoxide. The reaction is apparently due to the formation of a rather unstable carbonyl cuprous chloride, $CuCl \cdot CO \cdot 2H_2O$. A solution of cuprous ammonia carbonate is sometimes employed in place of the chloride for the same purpose. The chloride is soluble in cyanide and in ammonia, with the formation of the complex ions. The cyanide ion, $Cu(CN)_3^{--}$, gives the smallest concentration of cuprous ion of any of the cuprous compounds. **Cuprous sulfide** is formed by heating together copper and sulfur, by roasting cupric sulfide, and by reduction of cupric sulfide by hydrogen. It may also be precipitated from a solution of chlorcuprous acid by the action of hydrogen sulfide. It is soluble in hot nitric acid with the oxidation of both the copper and sulfur. **Cuprous thiocyanate,** CuCNS, is also insoluble.

9. Cupric Ion.—Cupric ion in dilute aqueous solution probably exists as $Cu(H_2O)_4^{++}$, and the characteristic blue color of its solutions is probably due to this complex. Its most important slightly soluble compounds are the black oxide, CuO; the green hydroxide, $Cu(OH)_2$; the green basic carbonate, $Cu_2CO_3(OH)_2$; the black sulfide, CuS; and red-brown ferrocyanide, $Cu_2Fe(CN)_6$. The most important complex ions are the deep blue cupric ammonia, $Cu(NH_3)_4^{++}$; chlor and brom cuprates, $CuCl_4^{--}$, $CuBr_4^{--}$ (respectively green and brown); and tartrate, $Cu\text{-}C_4H_2O_6^{--}$. The soluble cupric salts of strong acids are all slightly acid by hydrolysis.

10. Cupric Oxide and Hydroxide.—The addition of hydroxide ion to a cold solution of cupric ion gives a light bluish green gelatinous precipitate of the hydroxide, but in hot solutions the black oxide is formed. The oxide does not absorb water to form the hydroxide. The hydroxide is a weak base. It is not soluble in dilute alkalies, but does dissolve somewhat in 6*N* to 18*N*-NaOH, forming deep blue solutions of cuprate. The sodium cuprate, Na_2CuO_2, may be precipitated from the concentrated alkaline solutions. The hydroxide is soluble in ammonium hydroxide, forming the complex ammonia ion, and in tartrate, forming the complex tartrate (**Fehling's solution**). The oxide is

also formed by heating the carbonate or nitrate. At moderately high temperatures, it oxidizes hydrogen, forming water and copper. In quantitative organic analysis, mixtures of the oxide and organic compound are heated to effect the oxidation of the combined carbon and hydrogen to carbon dioxide and water.

11. Cupric Halides.—The fluoride, chloride, and bromide are readily soluble. As mentioned above, the iodide is unstable. The concentrated solution of the chloride is green, and of the bromide, brown. The color appears to be due to existence of part of the copper in the complex ions, $CuCl_4^{--}$ (yellow), and $CuBr_4^{--}$ (brown). Upon electrolysis, copper moves toward both the cathode and anode. When the concentrated solutions are diluted, the blue of the $Cu(H_2O)_4^{++}$ again predominates. The solid halides absorb ammonia gas to form compounds, such as $CuCl_2 \cdot 6NH_3$. These compounds, of course, give the complex ammonia ion upon solution.

12. Cupric Sulfate.—The sulfate is the most important copper salt. The anhydrous salt is colorless, but it readily absorbs water to form the blue pentahydrate, $CuSO_4 \cdot 5H_2O$, known as "blue vitriol." The five molecules of water of hydration may be successively replaced by ammonia. The sulfate is prepared commercially by roasting the sulfide, either to form the sulfate, which may be extracted with water, or to form the oxide, which may be dissolved in sulfuric acid. A 0.2*N* solution is 0.057 per cent hydrolyzed at 25° C. From solutions of copper sulfate and the alkali sulfates, double salts, such as $K_2Cu(SO_4)_26H_2O$, may be crystallized. Upon slow addition of alkali to copper sulfate solution, a number of insoluble basic sulfates are formed, for example, $Cu_5(SO_4)_2(OH)_62H_2O$. Basic sulfates, made by mixing copper sulfate and slaked lime, are used under the name of "**Bordeaux mixture**" as a fungicide. Copper sulfate is used in calico printing, in electroplating, and electrotyping, and as an electrolyte in the gravity battery. Copper is very poisonous to lower organisms, especially algae, and is used in swimming pools and water works to prevent the growth of such organisms.

13. Cupric Sulfide.—The brownish black sulfide is precipitated from cupric solutions by the action of hydrogen sulfide, even in the presence of high concentrations of acid. When precipitated from neutral solution, it may contain some cuprous sulfide. It is soluble in hot 2*N*-HNO_3 due to the oxidation of the sulfur,

and in cyanide ion due to the formation of $Cu(CN)_3^{--}$. The sulfide is slightly soluble in ammonium polysulfide, probably through the formation of thiocuprates.

14. Other Cupric Salts.—The **nitrate** crystallizes as blue hexahydrate. Because of the smaller solubility of the hydroxide, the normal carbonate does not exist, but two **basic carbonates,** azurite, $Cu_3(CO_3)_2(OH)_2$, and malachite, $Cu_2CO_3(OH)_2$, occur in nature. The latter is the green coating which forms on copper vessels through the action of oxygen and carbonic acid of the air. A **basic acetate,** verdigris, $Cu_3(C_2H_3O_2)_4(OH)_2$, is used as a green pigment. It is formed by the action of air upon copper in the presence of acetic acid. A mixed acetate and arsenite, $Cu_4(C_2H_3O_2)_2(AsO_3)_2$, **Paris green,** is used as an insecticide. Copper ferrocyanide, $Cu_2Fe(CN)_6$, may be formed as a brown gelatinous precipitate. It has been used in the preparation of semi-permeable membranes for studying osmotic pressure. **Copper phosphate,** $Cu_3(PO_4)_2$, is insoluble and is precipitated, together with basic phosphates, upon the addition of diammonium phosphate to a solution of copper sulfate.

15. Analytical.—Copper is recognized qualitatively by the intense blue color of the ammonia complex, and by the precipitation of the sulfide by hydrogen sulfide in acid solution. Nickel also gives a blue ammonia complex, but its sulfide is not precipitated in acid solution. A strip of iron in a not too acid copper solution will be coated with metallic copper. This is frequently a convenient and delicate test. The detailed methods of separation are indicated in Appendix VI. Copper is often determined quantitatively by the electrolytic precipitation of the metal in acid solution upon an accurately weighed cathode. This method affords a separation from the baser metals as well. A number of reactions are of importance in quantitative determinations. (*a*) $2Cu^{++} + 4I^- = 2CuI + I_2$. The liberated iodine is titrated with standardized thiosulfate. Other oxidizing agents such as ferric ion must be removed. (*b*) $2Cu(NH_3)_4^{++} + 7CN^- + H_2O = 2Cu(CN)_3^{--} + CNO^- + 2NH_4^+ + 6NH_3$. The ammonia solution is titrated with standardized cyanide to the disappearance of the blue color. This method is not as accurate as the iodide reaction. (*c*) $2Cu^{++} + 2CNS^- + SO_2 + 2H_2O = 2CuCNS + 4H^+ + SO_4^{--}$. The precipitate may be ignited and weighed as Cu_2S, or titrated with iodate in the presence of

concentrated hydrochloric acid: $4CuCNS + 7IO_3^- + 14H^+ + 14Cl^- = 4Cu^{++} + 4SO_4^= + 7ICl + 4HCN + 7Cl^- + 5H_2O$.

SILVER

16. Occurrence.—Native, or free silver is an important source of the element. It is usually alloyed with other of the noble metals. The most important naturally occurring compound is the sulfide, argentite, or silver glance, Ag_2S. It frequently occurs in solid solution with copper and lead sulfide, and as the sulfo-antimonite, Ag_3SbS_3, and arsenite, Ag_3AsS_3. The selenides and tellurides also occur. Silver chloride, AgCl, called horn silver, is an ore of some importance, and often contains the bromide and iodide in small amounts. The sulfate also occurs, being formed through the oxidation of the sulfide.

17. Metallurgy.—The recovery of silver from copper ores has been mentioned. Much of the lead smelted from lead sulfide contains silver. This is now recovered by Parke's process, which is essentially an extraction of the silver from the molten lead by means of zinc. Solid zinc is but slightly soluble in lead at temperatures just above the melting point of the latter. However, silver at these temperatures is about 3,000 times more soluble in the zinc than in the molten lead. Hence zinc in small amounts, usually 0.8 to 1.5 per cent, is stirred with the molten lead, and the greater portion of the silver is extracted. The zinc is removed from the silver by distillation. The small amount of lead present is removed by oxidation and absorption of the lead oxide on a cupel of bone ash.

The extraction of silver from comparatively pure silver ore is accomplished either by (1) amalgamation, or (2) leaching processes. The first depends upon the conversion of silver sulfide into chloride by copper chloride, $Ag_2S + Cu^{++} + 2Cl^- = 2AgCl + CuS$; and the decomposition of the chloride by mercury, $AgCl + Hg = Ag$ (amalgam) $+ HgCl$. The silver is recovered from the amalgam by distillation of the mercury.

A number of leaching processes have been employed. A sulfide ore may be roasted to convert the sulfide into sulfate, which may then be extracted with water. Or the sulfide may be roasted with salt to convert it into chloride, which is then leached, either with concentrated brine, the solubility being due to the formation of $AgCl_2^-$, or with thiosulfate, forming the

complex $Ag(S_2O_3)_2^{---}$. However, solutions of the alkali cyanides are now generally employed, as the metal and all of its compounds are readily dissolved by this reagent in the presence of air: $4Ag + 8CN^- + O_2 + 2H_2O = 4Ag(CN)_2^- + 4OH^-$; $Ag_2S + 4CN^- + \frac{1}{2}O_2 + H_2O = 2Ag(CN)_2^- + S + 2OH^-$; $AgCl + 2CN^- = Ag(CN)_2^- + Cl^-$. The silver is precipitated from the cyanide solution by zinc or aluminum.

18. The Metal.—The more important physical constants have been given in Table I. Silver is the most lustrous of all the metals. In thermal and electrical conductivity it also ranks among the first. It is but little inferior to gold in malleability and ductility. Silver melted in air always has a blistered surface upon cooling, due to the evolution of dissolved oxygen during solidification. The solubility of oxygen under 1 atmosphere pressure at the melting point is 20 volumes per volume of the metal. The cooled solid silver still contains 0.75 volume of oxygen.

TABLE V

REACTIONS OF THE METAL

$2Ag + \frac{1}{2}O_2 = Ag_2O$	At 200° with O_2 under pressure
$2Ag + X_2 = 2AgX$	X denotes any halogen
$2Ag + S = Ag_2S$	Also with Se and Te
$2Ag + H_2SO_4 = Ag_2SO_4 + SO_2 + H_2O$	Hot concentrated acid
$2Ag + 2H^+ + 2Cl^- + \frac{1}{2}O_2 = 2AgCl + H_2O$	
$2Ag + H_2O + 4CN^- + \frac{1}{2}O_2 = 2Ag(CN)_2^- + 2OH^-$	
$Ag = Ag^+ + E^-$	See oxidation reduction table

The annual production of silver is about 7,000 tons. Silver coins are generally 90 per cent silver with 10 per cent copper to increase the hardness. Jewelry usually contains 20 per cent of copper. The electroplating industry consumes a large proportion of the metal produced. The object to be coated is made the cathode in a cell containing a solution of sodium silver cyanide, $NaAg(CN)_2$, as electrolyte. The cyanide complex, which gives a very low concentration of silver ion, yields a much firmer deposit than solutions having a higher concentration of the silver ion. Frosted silver ornaments are obtained by roasting the object, made of the ordinary silver-copper alloy, to oxidize the copper on the surface to the oxide; this is dissolved in sulfuric

acid, leaving a layer of pure white silver. Silver mirrors are formed by precipitating the metal from a highly alkaline solution containing the silver ammonia complex ion by the aid of some organic reducing agent, such as glucose or formaldehyde. Approximately 150 tons of silver are used yearly in the production of photographic supplies.

19. Stability of Silver Compounds.—Silver ion is colorless. It forms such a very large number of slightly soluble salts and complexes that it is desirable to systematize the chemistry of these substances by arranging the more important in a list in order of decreasing concentration of silver ion in equilibrium with the solid or complex ion. (See Hildebrand, *Prin. of Chem.*, p. 204.) Ag_2O, Ag_2CO_3, Ag_2CrO_4, AgCl, $AgCl_2^-$, AgCN, $Ag(NH_3)_2^+$, AgBr, $AgBr_2^-$, $Ag(S_2O_3)_2^{--}$, AgI, AgI_2^-, $Ag(CN)_2^-$, Ag_2S. Any substance in the list may be formed at the expense of any substance preceding it. Thus silver iodide may be formed from the chloride: $AgCl + I^- = AgI + Cl^-$. Substances which are close together in the list may be present together in equilibrium at appreciable concentrations of both. Thus silver bromide is partially soluble in ammonium hydroxide, and the reaction is easily reversible, depending upon the concentration of ammonia and bromide. The dissociation constant for the ammonia complex ion is, $(Ag^+)\,(NH_4OH)^2/(Ag(NH_3)^+_2) = 6 \times 10^{-8}$.

The potentials of a number of silver complex ions and solids as oxidizing agents are given below. The decrease in oxidizing power is, of course, due to the decrease in concentration of silver ion.

	Volts
$Ag = Ag^+ + E^-$	-0.799
$Ag + BrO_3^- = AgBrO_3 + E^-$	-0.68
$2Ag + SO_4^{--} = Ag_2SO_4 + 2E^-$	$+0.65$
$Ag + C_2H_3O_2^- = AgC_2H_3O_2 + E^-$	-0.64
$2Ag + 2OH^- = Ag_2O + H_2O + 2E^-$	-0.58
$2Ag + CO_3^{--} = Ag_2CO_3 + 2E^-$	-0.50
$2Ag + C_2O_4^{--} = Ag_2C_2O_4 + 2E^-$	-0.47
$Ag + IO_3^- = AgIO_3 + E^-$	-0.37
$Ag + Cl^- = AgCl + E^-$	-0.22
$Ag + CNS^- = AgCNS + E^-$	-0.12
$Ag + Br^- = AgBr + E^-$	-0.08
$Ag + I^- = AgI + E^-$	$+0.14$
$Ag + 2CN^- = Ag(CN)_2 + E^-$	$+0.51$
$2Ag + HS^- + OH^- = Ag_2S + H_2O + 2E^-$	$+0.67$

20. Silver Oxide.—The brown oxide, Ag_2O, is precipitated by the addition of soluble alkalies to silver ion. The solid hydroxide is unstable and exists only momentarily. The oxide decomposes at comparatively low temperatures; the partial pressure of oxygen reaches 1 atmosphere at 184° C. However, the rate of decomposition does not become rapid until the oxide is heated much above this temperature. The decomposition is catalyzed by metallic silver. The oxide is distinctly basic in its reactions. It reacts with as weak an acid as carbonic to form the normal **carbonate,** Ag_2CO_3. As indicated above, the oxide is soluble in a large number of reagents with the formation of complex ions. The silver ammonia hydroxide, $Ag(NH_3)_2OH$, is a soluble strong base. Upon standing, the alkaline solution forms a highly explosive nitride, probably Ag_3N or Ag_2NH.

Peroxysulfuric acid oxidizes silver to the **sesquioxide,** Ag_2O_3. This trivalent oxide is a very powerful oxidizing agent and much less basic than the monovalent oxide. Strong oxidizing agents, in alkaline solution, appear to form the unstable oxide, AgO.

21. Silver Halides.—Silver fluoride is extremely soluble and forms a number of hydrates. The solubility of the other halides is very slight, decreasing with increasing molecular weight. Their solubility in various reagents has been indicated above. The solubility in excess halide to form the complexes, such as $AgCl_2^-$, requires a fairly high concentration of the halide. The chloride and bromide are not oxidized by nitric acid, but the iodide is. The halides form a number of solid ammoniates, such as $AgCl \cdot 3NH_3$. Silver chloride, however, is not very soluble in liquid ammonia. The photochemical properties of the halides are discussed under the subject of photography. The chloride and bromide have the so-called "sodium chloride" arrangement of the ions in the crystal, while the iodide has two forms, one the zinc oxide and the other the zinc sulfide arrangement (Append. V). The fluoride and chloride are colorless, but the bromide is light yellow and the iodide a deeper yellow. Silver chloride may be separated from the bromide by taking advantage of the difference in solubility in ammonia. A solution containing 32 g. of ammonia and 20 g. of silver nitrate per liter will dissolve the chloride, but not appreciable amounts of the bromide.

22. Silver Cyanide.—Silver cyanide is precipitated by addition

of cyanide, and forms the complex ion, $Ag(CN)_2^-$ or $Ag(CN)_3^-$, with excess of cyanide. The role of the silver cyanide complex ion in metallurgy and silver plating has been discussed. The complex gives the smallest concentration of silver ion of any of the silver compounds except the sulfide. From the electropotential given above it is evident that, in the presence of cyanide, silver is a powerful reducing agent.

23. Silver Nitrate.—The nitrate is prepared commercially by the action of nitric acid upon silver. The salt is extremely soluble. Its melting point is remarkably low, about 200° C.; cast into sticks it is used in medicine under the name of lunar caustic. At red heat, it is decomposed into metallic silver, oxygen, nitrogen, and nitrogen oxides. Many organic substances reduce it to finely divided metallic silver, as, for example, the black stains produced by the action of the salt upon the skin.

The salt is important in the preparation of other silver compounds. In dilute solutions it is used as an antiseptic, and in more concentrated solutions as a caustic. It is also used in indelible inks, especially in laundry markings.

24. Silver Sulfide.—The sulfide is the least soluble of all the silver salts. It is formed as a black precipitate by hydrogen sulfide, even in highly acid solutions. It is more stable toward decomposition upon heating than the oxide. Strong oxidizing agents dissolve it due to the oxidation of the sulfur. It is also somewhat soluble in concentrated cyanide ion. In the presence of air the reaction proceeds through the removal of the sulfide by oxidation to free sulfur. Metallic silver dissolves slowly in hydrogen sulfide with the evolution of hydrogen, $2Ag + H_2S = Ag_2S + H_2$, in accord with the large positive value for the $Ag - Ag_2S$ couple as given above.

25. Other Silver Salts.—In addition to those given above, the following slightly soluble compounds may be mentioned: the **phosphate,** Ag_3PO_4; **arsenite,** Ag_3AsO_3; **arsenate,** Ag_3AsO_4; **ferricyanide,** $Ag_3Fe(CN)_6$; and **dichromate,** $Ag_2Cr_2O_7$. **Silver nitrite,** $AgNO_2$, is but moderately soluble, and upon standing in contact with the solution decomposes according to the equation: $2AgNO_2 = Ag + Ag^+ + NO_3^- + NO$. The reaction is reversible. Silver ion also forms **alums,** such as $AgAl(SO_4)_2 \cdot 12H_2O$.

26. Photography.—The silver halides, as well as the cyanide, show marked changes when exposed to light, especially that of

the violet region of the spectrum. There is a change in color; white silver chloride, for example, becomes a deep greyish blue, and is decomposed into silver and the halogen. Many investigators have claimed the formation of **subhalides,** such as Ag_2Cl or Ag_4Cl_3, but it seems more probable that the action of the light is to cause an electron of the halide ion to pass more or less completely back to the silver without at first disrupting the crystal lattice of the ions. The result is essentially a solid solution of silver and atomic halogen in the halide, which, upon further exposure, slowly decomposes with evolution of the halogen. The halide which has been thus "activated" by light is acted upon much more readily by reducing agents than is the unexposed halide.

These photochemical reactions are the basis of the ordinary photographic processes. These may be divided into the following steps: preparation of the plate or film, exposure, development and fixation of the negative, and preparation of the positive, or print.

Dry plates or films are prepared by coating glass or celluloid with a colloidal suspension of silver bromide or chloride in gelatine. The operation must, of course, be carried out in the dark or in faint red light. The size of the particles of the silver halide affects the sensitivity of the plate to light; hence the suspension is warmed and allowed to "ripen" until the desired size of the grains is acquired.

The plate or film is exposed by projecting upon it momentarily an illuminated image. It is then developed by placing in a bath containing a reducing agent (various phenols, such as pyrogallol, metol, and hydroquinone are usually employed). The rapidity of reduction of the silver halide is proportional to the intensity of illumination falling upon it; and as a result the image on the plate is the "negative" of the original in that the bright portions are represented by heavy deposits of silver and the dark portions by faint deposits. The action of the reducing agent is stopped when the proper contrast is obtained, and the plate "fixed" by dissolving out the unreduced silver halide with sodium thiosulfate solution ("hypo").

The process of printing is essentially the same as making the negative, but since the sensitized paper is illuminated through the negative, the image is again reversed, and now appears with

the light and dark portions corresponding to the original. On the slower papers silver chloride suspension in albumen is used, while the faster papers, such as "velox," employ silver bromide in gelatine. The print may be toned by treating with solutions of sodium chloraurate, $NaAuCl_4$, or potassium chlorplatinite, K_2PtCl_4, which replace the precipitated silver by gold or by platinum. The former gives a red tone, and the latter dark grey.

"Orthochromatic" and "panchromatic" plates, more sensitive to the red, yellow, and green light, are prepared by adding to the gelatine various dyes, which absorb these longer wave lengths and thus utilize their energy for the activation of the silver halide.

27. Analytical.—Silver is detected by the precipitation of the chloride, insoluble in nitric acid, but soluble in ammonium hydroxide. It may be distinguished from the slightly soluble lead and mercurous chlorides by the fact that the former is soluble in hot water, but not in ammonia, while the latter turns black with ammonia. Silver is determined gravimetrically by precipitating and weighing as the chloride, bromide, or as the metal precipitated electrolytically. Silver may be titrated volumetrically with a solution of thiocyanate. Ferric ion is used as an indicator, since the deep red ferric thiocyanate is less stable than the silver salt, and the red color appears only when the silver has been almost completely precipitated. Silver is also titrated in dilute nitric acid with a standardized solution of alkali chloride or bromide, by taking advantage of the coagulation and settling of the precipitate with sufficient rapidity to permit the observation of any precipitate produced by further addition of the halide.

GOLD

28. Occurrence.—Gold is found in nature as the free metal, as the telluride, $AuTe_2$, and also as complex tellurides, e.g. $AuAgTe_4$. The sulfide, selenide, or chloride do not occur. Sea water contains gold to the extent of 0.01 to 0.3 part per million. The name reef gold is given to the deposits of gold occurring in quartz veins. Upon the weathering of the auriferous rocks, the gold has been washed into sand and gravel beds to form alluvial or placer deposits. Native gold nearly always contains silver and the platinum metals.

29. Metallurgy.—The richer deposits of gold have been worked for centuries by methods which recovered only the larger particles of the metal and which could not be applied to low grade ores. The crude methods of placer mining have been the simple agitation or washing of the gravel with water to bring about a separation of the heavy gold particles from the lighter materials. The use of mercury as an aid in the process by the amalgamation of the metal was probably introduced as early as 500 B.C.

The modern metallurgy of gold is quite similar to that of silver. Gold in copper and lead ores is recovered, along with the silver, by methods already discussed. The separation of the gold from the silver is known as "parting," and is usually carried out either by electrolytic methods or by the use of solvents, such as concentrated sulfuric or nitric acids, which dissolve the silver by oxidation, but not the gold. In the former case the impure metal is made the anode, with a solution of chlorauric acid as electrolyte. Pure gold deposits on the cathode. Silver is precipitated as the chloride together with the platinum metals in the anode mud. If excess silver is present, the electrolyte may be silver nitrate solution, in which case gold remains as sludge at the anode and silver deposited on the cathode.

The introduction of the cyanide process by Macarthur and Forrest about 1890 has contributed enormously to the world's gold supply through rendering available for commercial treatment low grade ores and also "tailings" from the amalgam process. The potential of the half reaction, $Au + 2CN^- = Au(CN)_2^- + E^-$, is about + 0.6 volt, that is, the gold in the presence of cyanide is a good reducing agent; hence by treating gold ore with a dilute cyanide solution in the presence of air, the metal is easily oxidized by the oxygen: $4Au + 8CN^- + O_2 + 2H_2O = 4Au(CN)_2^- + 4OH^-$. (Hydrogen peroxide appears to be formed as an intermediate step (cf. **III—4**). The reaction is not rapid and requires a number of days. The gold is precipitated from the solution by zinc or by electrolysis. High grade ores, after being pulverized in a mill, may first be washed over amalgamated copper plates to remove the larger gold particles which do not dissolve rapidly in the cyanide. The amalgam is scraped off the plates, and the gold recovered by distillation of the mercury.

30. The Metal.—The more important physical properties are

given in Table I. Gold is the most malleable and ductile of all metals. It may be rolled into sheets 0.00001 mm. thick and drawn into wire which weighs but 0.0005 g. per meter. The world's yearly production is about 1,000 tons. The gold used in jewelry is alloyed with copper. The copper alloys are redder, harder, and more fusible than pure gold. The temperature-composition curves for the alloy show a minimum melting point at 890° C. with a composition of 82 per cent gold. The purity of the metal is usually expressed in carats, that is, the number of parts of gold in 24 parts of the metal. The best jewelry is 15 to 18 carat gold. American coinage is 21.6 carat (90 per cent). Gold is deposited in electroplating from a solution of aurocyanide, and much cheap jewelry is manufactured by so depositing a very thin coat of gold on copper.

Gold is easily obtained in the **colloidal state**, especially in the presence of other stabilizing colloids. Thus, **purple of Cassius** is finely divided gold adsorbed on a hydrosol of stannic acid. The gold colloids may be formed by reduction of gold solution with chemical agents, or by electrical dispersion, using an arc between gold electrodes under water.

TABLE VI

REACTIONS OF METALLIC GOLD

$2Au + 3Cl_2 = 2AuCl_3$	At about 150°; also with Br_2
$Au + 2Te = AuTe_2$	
$Au + 6H_2SeO_4 = Au_2(SeO_4)_3 + 3SeO_2 + 6H_2O$	
$Au + 5H^+ + 4Cl^- + NO_3^- = HAuCl_4 + NO + 2H_2O$	Solution in Aqua regia
$2Au + 4CN^- + \frac{1}{2}O_2 + H_2O = 2Au(CN)_2^- + 2OH^-$	
$2Au + 2Na_2S_2 = 2NaAuS_2 + Na_2S_2$	

31. Equilibria between Valence States.—Aurous ion is unstable in respect to the decomposition: $6Au^+ + 3H_2O = 4Au + Au_2O_3 + 6H^+$ (about 0.3 volt); hence only those aurous compounds and complexes which are relatively less soluble and less ionized than the corresponding auric compound can be prepared in solution. The only aurous compound which appears to be really stable with respect to the auric in solution is the aurocyanide: $Au(CN)_4^- + 2Au + 2CN^- = 3Au(CN)_2^-$.

Oxidation reduction potentials are summarized in Table VII. The value given for the formation of aurocyanide, + 0.6 volt, may be too high, as gold does not appear to dissolve in cyanide solution with the evolution of hydrogen.

TABLE VII

OXIDATION REDUCTION POTENTIALS OF GOLD

	Volts$_{25°}$
$Au = Au^{+} + E^{-}$	about − 1.5
$Au + 2CN^{-} = Au(CN)_2^{-} + E^{-}$	+ 0.6
$2Au + 3H_2O = Au_2O_3 + 6H^{+} + 6E^{-}$	− 1.36
$Au + 4Cl^{-} = AuCl_4^{-} + 3E^{-}$	− 1.0

Auric chloride and bromide decompose upon heating to give the aurous halide: $AuCl_3 = AuCl + Cl_2$. Many of the auric compounds, however, decompose, giving the metal. A number of divalent compounds also exist, but they are all unstable with respect to the reaction, $3Au^{++} = Au + 2Au^{+++}$.

32. Oxides.—The aurous oxide, Au_2O, is said to be formed by the action of dilute potassium hydroxide upon aurous chloride, but it is very unstable and, in excess hydroxide, gives the metal and aurate, AuO_2^{-}. The addition of hydroxide to auric solutions gives a precipitate of $Au(OH)_3$, which, when dried gently, gives the sesquioxide, Au_2O_3. This is amphoteric, and is somewhat more acidic than basic. The alkali aurates, such as $KAuO_2$, are soluble; but those of the alkaline earths are not. The oxide forms with ammonia the highly explosive gold "**fulminate,**" probably $AuN \cdot NH_3$. An unstable divalent oxide, AuO, is also known.

33. Halides.—Fluorine does not attack gold at ordinary temperatures, but at higher temperatures a slight reaction occurs. The fluoride is completely hydrolyzed by water, forming auric hydroxide. Chlorine attacks gold in the neighborhood of 150°, forming $AuCl_3$. At somewhat higher temperatures the aurous chloride, AuCl, is formed. This is but slightly soluble in water. Both chlorides are soluble in excess hydrochloric acid, forming, respectively, $HAuCl_4$ and $HAuCl_2$. The latter is unstable, as discussed above. Auric chloride is usually prepared by the action of **aqua regia** upon gold. Sodium chloraurate, $NaAuCl_4 \cdot 2H_2O$, is employed in photography in toning prints. The two bromides, AuBr and $AuBr_3$, are analogous in most respects to the chlorides. Gold is slowly attacked by iodine at 50°, forming AuI. The aurous iodide is also formed by the reaction: $Au_2O_3 + 6HI = 2AuI + 3H_2O + 2I_2$. Auric iodide is very unstable.

34. Sulfides.—Gold and sulfur do not unite when heated together, but gold is dissolved by molten alkali polysulfides, forming thioaurites and possibly some thioaurates. Hydrogen sulfide in warm acid solution gives with $AuCl_4^-$ a precipitate of gold and sulfur. In cold solution some of the unstable sulfides, Au_2S and AuS, appear to be formed.

35. Other Compounds.—Mention has been made of the occurrence of gold **telluride**, and also of the stability and importance of the **cyanoaurites.** The alkali cyanoaurites, such as $KAu(CN)_2$, are soluble. Auric nitrate and sulfate are so highly hydrolyzed that auric oxide is soluble only in very concentrated solution of these acids.

36. Analytical.—The presence of auric gold may be determined by the rose coloration (colloidal gold) produced upon the addition of a dilute solution of stannous chloride to the auric solution in excess hydrochloric acid. Gold, in the form of auric chloride, is sometimes determined quantitatively by the reaction, $AuCl_4^- + 3I^- = AuI + I_2 + 4Cl^-$, the liberated iodine being titrated with thiosulfate (cf. **X—20**). Gold ores are usually analyzed by the fire assay. The first step in the assay is the separation of the gangue, and the concentration of gold and silver in a lead "button." This operation may be carried out in a shallow clay dish called a "scorifier," in which the sample of ore is heated with a large amount of lead and a little borax. Much of the lead is oxidized, and the oxide forms an easily fusible flux with the silicates and borates. The rest of the lead serves to collect the gold and silver, and when the molten mass is cooled the lead is found as a small lump or button which may be separated from the slag. This process is sometimes carried out in a crucible with a mixture of ore, fluxing agent, lead oxide, and some reducing agent. The latter reduces some of the lead oxide, and the metal collects the gold and silver as in the scorification process. The second step is the separation of the gold and silver from the lead. The button is heated in a little cup of bone ash called a "cupel." The lead oxidizes, and the liquid oxide is readily absorbed by the bone ash, while the liquid gold and silver remain in a small globule. The third step is the "parting" of the gold and silver. The button is flattened by hammering and treated with nitric acid to dissolve out the silver. Unless there is a considerable excess of silver, more must be added before the

separation can be accomplished, as otherwise the silver atoms are removed from the surface of the button but the crystal lattice is not destroyed, and the action soon stops. However, if there is a large excess of silver, the crystal is completely disintegrated, and the finely divided gold remaining may be fused and weighed.

CHAPTER VIII

SUBGROUP II. ZINC, CADMIUM, AND MERCURY

1. The elements of Subgroup II, zinc, Zn, cadmium, Cd, and mercury, Hg (hydrargyrum), differ from the elements of the main group in much the same way that copper, silver, and gold differ from the alkali metals. Thus the subgroup elements are more noble, their hydroxides are less basic, and their ions have a greater tendency to form complex ions. These properties depend upon the much higher ionization potentials of the atoms and the smaller size of the resultant ions (Table I). The melting points of the elements in Subgroup II are much lower than those of the main group. They all form divalent positive ions, but in addition, mercury forms an unusual series of compounds of the ion, Hg_2^{++}, and cadmium appears to form the monovalent chloride and oxide. These elements are less noble than the corresponding elements of Subgroup I, and their hydroxides are more acidic.

Zinc and cadmium resemble each other much more closely than they do mercury. They are distinctly electropositive, are readily oxidized by hydrogen ion, and their oxides are reduced with difficulty; while mercury is a noble metal, and its oxide is easily decomposed upon simple heating. The solubility of the oxide in water increases with increasing size of the metal ion. Zinc oxide is amphoteric, dissolving readily in both acids and bases. Cadmium and mercuric oxides dissolve in acids, and unstable cadmates and mercurates are also known. Both zinc and cadmium form stable hydroxides, but mercury does not. Mercuric salts are very highly hydrolyzed, notwithstanding the appreciable solubility of mercuric oxide. One of the outstanding characteristics of the subgroup is the slight dissociation of the chlorides, bromides, and iodides. This property is most pronounced with the mercuric ion. In the most stable salts and complexes, the apparent ionic radii are 10 or 15 per cent less than the values given in Table I, as the high attractive force is able to distort the ions from their normal shapes (cf. **VII—2**).

TABLE I

ATOMIC AND PHYSICAL PROPERTIES OF ZINC, CADMIUM AND MERCURY

	Zn	Cd	Hg
Atomic number	30	48	80
Atomic weight	65.38	112.41	200.61
Isotopes	64, 66, 68, 70	110, 111, 112, 113, 114, 116	197, 199, 200, 201, 202, 204
Electrons in various quantum levels, 1st	2	2	2
2d	8	8	8
3d	18	18	18
4th	2	18	32
5th		2	18
6th			2
Radius of M^{++} in crystals $\times 10^8$ cm. (if $Cl^- = 1.81$)	0.74	0.97	1.10
Ionization potential of gaseous atoms in volts, 1st electron	9.35	8.95	10.39
2d electron	27.56	26.26	30.00
Melting point ° C.	419.4	320.9	− 38.8
Boiling point ° C.	907	767	356.9
Density of solids	7.14	8.6	14.19 at − 40°
Electrical resistance ohm-cm. $\times 10^6$	6	7.5 at 20°	21.3 at − 50°
Potential of electrode: $M = M^{++} + 2E^-$ in volts	+ 0.758	+ 0.397	− 0.86
Solubility of $Zn(OH)_2$, $Cd(OH)_2$ and HgO, g. per liter	2.6×10^{-6}	2.6×10^{-4}	5×10^{-2}

ZINC AND CADMIUM

2. Occurrence.—The principal zinc ores are the sulfide, ZnS, called sphalerite or zinc blende; and the carbonate, $ZnCO_3$, smithsonite. Other ores are: willemite, Zn_2SiO_4; calamine, $Zn_2H_2SiO_3$; zincite, ZnO; and franklinite, $[Fe, Zn, Mn](FeO_2)_2$.

Most zinc ores contain some cadmium. The average ratio of zinc to cadmium is about 200 to 1. The yellow cadmium sulfide sometimes occurs fairly pure and is known as greenockite.

3. Metallurgy.—The major portion of the zinc ore is smelted by reduction with carbon, although more than a hundred thousand tons of pure zinc are now produced yearly by a process which combines the extraction of the ore by leaching, and the

electrolytic reduction of the metal from the solution. In the former process the ore is first crushed and concentrated by washing out the lighter rocks, or, in the case of the sulfide, by "flotation" methods (see Metallurgy of Lead). Sulfide and carbonate ores are roasted to convert them into the oxide: $2ZnS + 3O_2 = 2ZnO + 2SO_2$. Much of the sulfur dioxide liberated is recovered and made into sulfuric acid. The oxide is mixed with coal, and the mixture heated in small clay retorts (4 to 5 feet long). A temperature of 1,200 to 1,300° C. is required for reduction, and as the boiling point of the metal is only 907°, the metal is vaporized as soon as it is liberated: $ZnO + C = Zn + CO$. A sufficient excess of coal is employed to prevent the formation of carbon dioxide, since zinc is oxidized by the dioxide. A small condenser is placed over the mouth of the retort, and its temperature is controlled so as to condense the metal to the liquid state. If the temperature of the condenser is below the melting point of the zinc, the metal collects in the form of a fine powder called zinc dust, which also contains a small per cent of zinc oxide. Even under the best conditions, some zinc dust is formed, and 10 per cent or even more of the zinc escapes from the condenser along with the carbon monoxide. The liquid is drawn off and cast into moulds, forming what is known as "spelter." It usually contains, as the principal impurities, a per cent or so of lead and smaller amounts of iron and cadmium. The metal may be purified by distillation in vacuum or in hydrogen, but it is difficult to effect a complete separation from the lead.

In the electrolytic process sulfide ore is first carefully roasted at a low temperature, and under these conditions forms largely sulfate. The ore is then leached with dilute sulfuric acid, and the acid sulfate solution treated with a small quantity of zinc dust to precipitate the nobler metals, as these would deposit along with the zinc upon electrolysis of the solution. Although the potential required to precipitate zinc is 0.758 volt greater than the reversible reduction potential for hydrogen ion, the overvoltage of hydrogen on pure zinc is sufficiently great (1.23 volts in $1N$ H^+) to permit the deposition of zinc in acid solution if a high cathodic current density is used. Electrolytic zinc is very pure, and commands a higher price for that reason. The annual production of zinc is over a million tons.

Cadmium is both more easily reduced and more volatile than zinc; consequently, it is concentrated in the first portions of the distillate in zinc smelting, and may be recovered from the zinc by fractional distillation. However, most of the commercial product now comes from the electrolytic zinc process, the cadmium being precipitated along with the more noble metals in the purification of the electrolyte.

4. The Metals.—The more important physical properties have been summarized in Table I. Zinc takes a good white metallic luster upon polishing, but the surface quickly tarnishes to the familiar blue-grey tinge. Zinc is hard and brittle at ordinary temperatures, but between 100° and 150° it becomes malleable enough to permit rolling and drawing. At somewhat higher temperatures, it becomes so brittle that it may be pulverized in a mortar. These changes appear to be due to allotropic forms, but the transitions from one form to another have not been definitely determined.

Zinc is used in making brass (see Copper) and many other alloys. It is used in dry cells (see Manganese) and the preparation of zinc pigments (see Oxide, Sulfate, and Sulfide). The largest use of the metal, however, is in galvanizing iron. The process is carried out in three different ways: (1) dipping the iron into molten zinc, (2) depositing the zinc upon the iron by electrolytic reduction, (3) exposing the iron to the action of zinc vapour, called "sherardizing." Galvanized iron resists the action of weather better than pure iron, largely due to the impervious coating of basic zinc carbonate on the surface, but in part to the fact that the electropositive character of the zinc tends to prevent a hole wearing through the iron by furnishing electrons in place of the iron. Zinc dust is employed as a reducing agent in the manufacture of dyes.

Cadmium has a silver white color with a slight bluish tinge. It is not as hard as zinc, and at ordinary temperatures is much more ductile and malleable. Like zinc, however, it becomes very brittle at higher temperatures, the change likewise appearing to be due to a crystalline transition. The electrical conductivity of cadmium is somewhat less than that of zinc.

Cadmium is used as a substitute for tin in antifriction metals and solders. Its presence in small amounts in copper wire adds strength with but small reduction in the conductivity. Cadmium

plating is now used to rust-proof wires, tools, and other iron and steel articles. After plating, the articles are heat-treated, thus alloying the cadmium and iron.

5. Reactions of the Metals.—Zinc dust is subject to spontaneous combustion in moist air, but in more compact forms does not burn readily until heated above 500° C. Pure zinc is almost insoluble in dilute hydrogen ion, due to the very large overvoltage of the hydrogen. If, however, the metal be touched with some metal with a low overvoltage for hydrogen, such as nickel or platinum, the evolution of hydrogen takes place rapidly on the surface of the other metal, and the zinc dissolves. The high positive value of the oxidation-reduction potential (Table I) renders it possible to dissolve zinc by a number of oxidizing agents. The metal is soluble in rather concentrated alkali with the evolution of hydrogen and formation of zincate. These and other reactions are summarized in Table II.

TABLE II

REACTIONS OF ZINC METAL

$2Zn + O_2 = 2ZnO$	Upon heating
$Zn + 2H^+ = Zn^{++} + H_2$	Slow with pure zinc
$Zn + 2H_2O = Zn(OH)_2 + H_2$	With steam at high temperature
$Zn + OH^- + H_2O = HZnO_2^- + H_2$	With concentrated alkali
$Zn + S = ZnS$	Also with Se, Te, P, As, etc.
$Zn + X_2 = ZnX_2$	X is any halogen
$Zn = Zn^{++} + 2E^-$	0.758 volt
$Zn + CO_2 = ZnO + CO$	At red heat
$4Zn+2O_2+3H_2O+CO_2=Zn_4CO_3(OH)_6$	The protective coating on zinc surfaces

The reactions of cadmium are, in general, similar to those of zinc, but the lower positive value of the oxidation reduction couple, 0.397 volt, renders it considerably less reactive with oxidizing agents. Unlike zinc, it does not dissolve in alkali.

6. Zinc and Cadmium Ions.—The ions Zn^{++} and Cd^{++} are colorless and poisonous to most organisms, cadmium more so than zinc. Zinc ion is rather highly hydrolyzed, while cadmium ion is only slightly so. Zinc ion forms as its more important slightly soluble compounds: $Zn(OH)_2$, $ZnCO_3 \cdot nZn(OH)_2$, $ZnNH_4PO_4$, $Zn_3(PO_4)_2$, ZnP_2O_7, ZnC_2O_4, $Zn(CN)_2$, $Zn(IO_4)_2$, $Zn_2Fe(CN)_6$, and ZnS. Its most stable complex ions are $Zn(NH_3)_4^{++}$, $Zn(CN)_4^{--}$, and $HZnO_2^-$. Cadmium ion forms the

precipitates: $Cd(OH)_2$, $CdCO_3 \cdot nCd(OH)_2$, $Cd(CN)_2$, $Cd_2Fe(CN)_6$, and CdS; and the complex ions, $Cd(NH_3)_4^{++}$, $Cd(CN)_4^{--}$, and CdI_4^{--}.

7. Oxides and Hydroxides.—Zinc oxide, ZnO, occurs as the mineral zincite. It is an important commercial commodity, and is prepared by the oxidation of the metal or directly from the oxidized ores by heating a mixture of carbon and ore in an air blast. The carbon reduces the oxide, but the zinc vapor is immediately reoxidized, and the oxide carried along as a fine dust in the flue gas, from which it is finally recovered by the use of filter bags. This oxide is used extensively as a white pigment, generally mixed with white lead. It is employed in the manufacture of automobile tires, and in medicine as a base for various ointments. It may be formed by gently heating the hydroxide, but it will not combine with water to form the hydroxide. It is yellow when hot, and white when cold. The arrangement of the zinc and oxide ions in the crystal lattice is given in Appendix V.

The hydroxide is precipitated upon the addition of hydroxide ion to a solution of zinc ion. It is amphoteric, and readily soluble in excess hydroxide and in acids: $Zn(OH)_2 + OH^- = HZnO_2^- + H_2O$; and $Zn(OH)_2 + 2H^+ = Zn^{++} + 2H_2O$. The solid zincates, such as K_2ZnO_2, are prepared by fusion of the two oxides, but are highly hydrolyzed in solution. Zinc hydroxide is soluble in ammonium hydroxide, due to the stability of the complex, $Zn(NH_3)_4^{++}$. Peroxides in alkaline solution form with zinc salts the hydrated zinc peroxide, $ZnO_2 \cdot 2H_2O$.

The brown cadmium oxide, CdO, is formed by methods similar to those discussed for zinc oxide. Cadmium hydroxide is more soluble and more basic than zinc hydroxide. It does not dissolve in excess hydroxide ion, but cadmates are said to be formed by fusing cadmium oxide in potassium hydroxide. Cadmium hydroxide is soluble in ammonium hydroxide, and in alkali iodides and cyanides with the formation of the complex ions: $Cd(NH_3)_4^{++}$, CdI_4^{--}, and $Cd(CN)_4^{--}$. A hydrated cadmium peroxide similar to the zinc peroxide exists, and **cadmous hydroxide,** CdOH, appears to form when a base is added to the unstable cadmous chloride. The hydroxide is a powerful reducing agent.

8. Halides.—Although zinc and cadmium fluorides are but

moderately soluble, the other halides are readily soluble. They crystallize from their solutions as hydrated salts, usually with 4 moles of water at low temperatures, and one mole at higher temperatures. Solutions of the zinc salts are distinctly acid by hydrolysis, and readily precipitate basic halides upon the addition of dilute alkali. Concentrated solutions of zinc chloride dissolve zinc oxide and set to form a cement, ZnOHCl, similar to the magnesia cement. The chloride in the fused state also dissolves metal oxides, and is much used as a flux in soft soldering.

In their concentrated solutions, the halides appear to be slightly ionized, due to the formation of complex ions. This property is exhibited somewhat by the zinc salts and markedly by the cadmium. The latter forms, for example, $CdCdCl_4$ and $CdCdF_4$. The complex ion, CdI_4,— is so extremely stable that all of the cadmium compounds are soluble in excess sodium iodide.

Cadmous chloride, CdCl, appears to be formed by heating the dichloride and metal together at about 800°. It is hydrolyzed by water to CdOH.

9. Sulfates.—The crystallization of an aqueous solution of zinc sulfate at ordinary temperature forms the heptahydrate, $ZnSO_4 \cdot 7H_2O$; and solutions of cadmium sulfate form the hydrate, $3CdSO_4 \cdot 8H_2O$. A number of other hydrates also occur at higher and lower temperatures. These hydrates are very soluble in water. Large quantities of zinc sulfate are used in the preparation of the white pigment, **lithopone,** the reaction being: $ZnSO_4 + BaS = BaSO_4 + ZnS$. This pigment does not blacken with hydrogen sulfide, as does white lead, and possesses fair covering power. Cadmium sulfate is employed in the manufacture of "standard cells" for electrical measurements. These cells have an anode of cadmium amalgam, a cathode of mercurous sulfate in contact with mercury, and an electrolyte of cadmium sulfate solution.

10. Sulfides.—Zinc sulfide is the only common white metallic sulfide. Cadmium sulfide is yellow. Zinc sulfide is precipitated by the addition of alkali or ammonium sulfides to solutions of zinc salts. Its solubility is increased by hydrogen ion: $ZnS + H^+ = Zn^{++} + HS^-$; but it may be fairly completely precipitated in a solution of acetic acid with sodium acetate added to reduce the hydrogen ion concentration. Cadmium sulfide is

much less soluble, and may be precipitated from highly acid solutions. Neither sulfide is soluble in excess of sulfide ion, but both are slightly soluble in high concentrations of ammonium hydroxide, due to the formation of the complex ammonia ions. Cadmium sulfide is also soluble in iodide, as mentioned under the halides, but it is not soluble in cyanide. Cadmium sulfide is an excellent yellow pigment, but is too expensive for extensive application.

11. Other Salts.—The **nitrates** are readily prepared by dissolving the metals or oxides in nitric acid. Normal **zinc carbonate** exists in nature, but basic carbonates are precipitated from solution by the alkali carbonates. Cadmium shows less tendency to form basic carbonates than does zinc. The physical properties of a number of other compounds are included in Appendix XIX.

12. Analytical.—The separation of zinc and cadmium from other metallic elements is indicated in the standard scheme of analysis (Append. VI). The separation of aluminum from zinc, by the precipitation of aluminum hydroxide with excess ammonium hydroxide, carries down considerable zinc as zinc aluminate, and, for this reason, in detecting small amounts of zinc, it is preferable to precipitate the aluminum as $AlCl_3 \cdot 6H_2O$, by adding ether and hydrogen chloride gas. The insolubility of cadmium sulfide in excess sulfide ion distinguishes it from arsenic, antimony, and tin; and its solubility in hot nitric acid gives a separation from mercuric sulfide. The precipitation of cadmium sulfide in the presence of cyanide ions serves to distinguish cadmium from copper.

Zinc may be determined quantitatively by precipitating as the sulfide, igniting and weighing as the oxide; by precipitation as $ZnNH_4PO_4$, and weighing as $Zn_2P_2O_7$; or by precipitation by cathodic reduction from an acetic acid-acetate buffer solution. In the electrolytic determination, it is difficult to obtain a complete precipitation of the metal. The most satisfactory volumetric method is the titration of zinc with ferrocyanide. The formation of a brown color with a uranyl solution as an outside indicator is used to determine the end-point, or a few drops of ferrous ion may be added to the zinc solution, in which case the color changes from light blue to pea-green at the end-point. This latter color change appears to be due to the presence

of a trace of ferricyanide, which gives a blue color until an excess of ferrocyanide is obtained.

Cadmium may be determined gravimetrically by precipitating as carbonate and weighing as oxide; or, similarly to zinc, precipitating as phosphate and weighing as $Cd_2P_2O_7$. It is impossible to precipitate the sulfide pure enough to weigh as such, as it forms complexes, e.g. Cd_2Cl_2S. Cadmium may also be determined electrolytically by reduction from a solution of the cyanide complex.

MERCURY

13. Occurrence.—Mercury occurs native and in amalgams of gold and silver, but the principal ore is cinnabar, HgS. Complex selenides, tellurides, and chlorides also occur, but they are of slight economic importance.

14. Metallurgy.—The extraction of mercury from the sulfide ore is comparatively simple, since the sulfide may readily be converted into the volatile metal, either by roasting in air: $HgS + O_2 = Hg + SO_2$; or by roasting with lime: $4HgS + 4CaO = 3CaS + CaSO_4 + 4Hg$. The mercury vapor is more easily condensed from the furnace gases than is zinc, because of the greater weight of the molecules of vapor, and also because the vapor is not readily reoxidized by air. The metal is filtered through chamois skin and purified by washing with nitric acid, or mercurous nitrate solution; or by distillation in the presence of oxygen, or other oxidizing agents, which will remove the base metals, especially zinc and cadmium.

15. The Metal.—The more important physical properties have been given in Table I. The metal is a silvery-white liquid with a vapor pressure of 0.001 mm. at 20° and 0.28 mm. at 100°. Its boiling point is 356.90°. A table of densities of the liquid is given in Appendix IX. The vapour is monatomic, and does not conduct electricity in the cold, but if an arc is once struck it conducts readily with the emission of the characteristic mercury spectrum which is very rich in green and ultra-violet light. This mercury vapor arc is much used as a current rectifier, and as a source of ultra-violet light for the treatment of certain diseases. The cubical coefficient of expansion of mercury between 0° and 300° is represented by the expression: $\alpha = 1.8006 \times 10^{-4} + 2 \times 10^{-8}t$. Due to this rather uniform expansion and

to the fact that the pure liquid does not "wet" glass, mercury is extensively used in thermometers. Its low vapor pressure and high density makes it useful in barometers. With the exception of iron and platinum, metals readily dissolve in, or are wet by mercury to form amalgams; many of these have been mentioned in connection with other metals, e.g. sodium, aluminum, gold, and silver. Amalgams of tin, silver, gold, and other metals are employed in dentistry. Many attempts have been made to use mercury in heat engines, as the higher boiling point offers a very substantial increase in the theoretical efficiency over the steam engine.

TABLE III

REACTIONS OF THE METAL

$2Hg + O_2 = 2HgO$	Slowly around 350°
$Hg + X_2 = HgX_2$	X is any halogen
$Hg + S = HgS$	Upon subliming together
$3Hg + 2NO_3^- + 8H^+ = 3Hg^{++} + 2NO + 4H_2O$	Excess acid
$6Hg + 2NO_3^- + 8H^+ = 3Hg_2^{++} + 2NO + 4H_2O$	Excess mercury
$Hg + SO_4^{--} + 4H^+ = Hg^{++} + SO_2 + 2H_2O$	Hot concentrated acid

16. Equilibria between Valence States.—The mercurous ion is stable in respect to the decomposition into mercuric ion and mercury: i.e. mercuric ion is reduced by mercury: $Hg^{++} + Hg = Hg_2^{++}$, with a potential of about 0.06 volt. However, this value for the potential of the reaction corresponds to an equilibrium concentration of Hg_2^{++} at 25° C., only about 100 times that of Hg^{++}; hence the equilibrium is easily reversed in case the mercuric compound is much less soluble than the mercurous: e.g. $Hg_2S = HgS + Hg$ and $Hg_2O = HgO + Hg$. Due to the insolubility of the basic ammonia mercuric salts (Par. 25), all mercurous compounds are decomposed by ammonia. The equilibrium lies in the direction of the mercuric form at higher temperatures. In this respect the higher valence state is different from copper, since cupric oxide upon heating gives cuprous oxide and oxygen, while mercuric oxide gives mercury and oxygen. Mercuric sulfate, however, decomposes at high temperatures according to the equation: $2HgSO_4 = Hg_2SO_4 + SO_2 + O_2$.

The couple Hg^{++}-Hg^+ is a stronger oxidizing couple than Hg^{++}-Hg (Table IV); hence reducing agents first reduce mercuric ion to mercurous. Since the potential of the couple Hg^+-Hg is

almost as large, most reducing agents capable of reducing mercuric ion will, in excess, reduce the mercurous ion to mercury as a second step: e.g. $2Hg^{++} + Sn^{++} = 2Hg^{+} + Sn^{++++}$, and $2Hg^{+} + Sn^{++} = 2Hg + Sn^{++++}$. It also follows from the potential values that fairly powerful oxidizing agents, e.g. bromine water and hot nitric acid, are required to oxidize mercurous compounds to mercuric, unless, of course, the mercuric compound is much less soluble or less ionized.

TABLE IV

OXIDATION-REDUCTION POTENTIALS OF MERCURY

	$Volts_{25°}$
$Hg + HS^{-} + OH^{-} = HgS + H_2O + 2E^{-}$	+ 0.77
$Hg + 4CN^{-} = Hg(CN)_4^{--} + 2E^{-}$	+ 0.37
$Hg + 4I^{-} = HgI_4^{--} + 2E^{-}$	+ 0.05
$2Hg + 2I^{-} = Hg_2I_2 + 2E^{-}$	+ 0.04
$Hg + 2OH^{-} = HgO + H_2O + 2E^{-}$	− 0.099
$2Hg + 2Br^{-} = Hg_2Br_2 + 2E^{-}$	− 0.14
$2Hg + 2SCN^{-} = Hg_2(SCN)_2 + 2E^{-}$	− 0.22
$2Hg + 2Cl^{-} = Hg_2Cl_2 + 2E^{-}$	− 0.270
$2Hg + CO_3^{--} = Hg_2CO_3 + 2E^{-}$	− 0.33
$2Hg + CrO_4^{--} = Hg_2CrO_4 + 2E^{-}$	− 0.38
$2Hg + C_2O_4^{--} = Hg_2C_2O_4 + 2E^{-}$	− 0.44
$2Hg + SO_4^{--} = Hg_2SO_4 + 2E^{-}$	− 0.621
$Hg_2Cl_2 + 2Cl^{-} = 2HgCl_2 + 2E^{-}$	− 0.63
$2Hg = Hg_2^{++} + 2E^{-}$	− 0.798
$Hg = Hg^{++} + 2E^{-}$	− 0.86
$Hg_2^{++} = 2Hg^{++} + 2E^{-}$	− 0.92

MERCUROUS COMPOUNDS

17. Mercurous ion is strikingly similar to silver ion in the solubility of its salts, and in the potential of reduction to the metal. However, the mercurous ion is peculiar in that it is associated into the double ion, Hg_2^{++}, not only in solution, but in its compounds in the solid and gaseous state. Indeed it is somewhat doubtful if the undissociated ion Hg^{+} exists. From the standpoint of atomic structure, the mercurous ion is quite unusual. The variable valence of the Subgroup I metals arises through the possibility of removing electrons from the kernel, but the mercurous ion consists of the kernel plus one valence electron. Many examples may be given of the association of molecules containing an odd number of electrons; and the formation of $(\mathbf{Hg : Hg})^{++}$ may be correlated with this general behavior of "odd" molecules. The mercurous ion does not form

complex ions with the ammonia, cyanide, iodide, or thiosulfate, as does silver ion.

18. Mercurous oxide, Hg_2O, is formed by the action of alkalies upon soluble mercurous salts. It is not soluble in excess hydroxide ion. The oxide decomposes slowly at 25°, and rapidly at 100°, into mercury and mercuric oxide. The speed of decomposition is increased by light.

19. Mercurous chloride, Hg_2Cl_2, or calomel, is the most important mercurous salt. It is usually prepared by subliming a mixture of mercuric chloride and mercury: $HgCl_2 + Hg = Hg_2Cl_2$. It is formed as a white precipitate by the addition of chloride to a solution of mercurous nitrate. Mercurous chloride sublimes without melting, and if dry, the vapor consists of Hg_2Cl_2 molecules, but moisture catalyzes its decomposition into mercury and mercuric chloride. Light causes a partial decomposition of the salt at room temperature. Mercurous chloride turns dark when treated with ammonia, due to the formation of finely divided mercury and the ammono-basic mercuric chloride (Par. 25). The use of calomel in medicine depends upon its stimulating action upon the liver and other secretive organs. The potential of the reaction: $2Hg + 2Cl^- = Hg_2Cl_2 + 2E^-$ is 0.2700 volt (i.e. in normal chloride ion and referred to the potential of hydrogen arbitrarily chosen as zero); and the electrode: mercury—solid mercurous chloride—chloride ion, is often employed as a reference electrode in potential measurements. Much work has been done on the absolute value of this electrode potential, and the value 0.56 volt is usually accepted; the mercury is positive with respect to the solution.

20. Mercurous fluoride, bromide, and iodide resemble the corresponding silver salts in respect to solubility in water. The iodide is unstable, especially with excess iodide, and decomposes into mercury and mercuric iodide.

21. Mercurous sulfide may be formed momentarily by the action of hydrogen sulfide upon mercurous salts, but it immediately decomposes into mercury and mercuric sulfide. **Mercurous nitrate** and **sulfate** may be prepared by the action of nitric acid and of hot concentrated sulfuric acid, respectively, upon excess mercury. The nitrate is readily soluble, but the sulfate only sparingly so. Both are hydrolyzed, and unless excess acid is

present, form slightly soluble basic salts, such as $Hg_2(OH)NO_3$ and $HgOHg_2SO_4 \cdot H_2O$.

Mercurous phosphate, nitrite, chromate, bromate, and **iodate,** are but slightly soluble. Alkali carbonates precipitate **mercurous carbonate** from soluble mercurous salts. The carbonate is unstable if warmed slightly: $Hg_2CO_3 = Hg + HgO + CO_2$. **Mercurous cyanide** is not stable.

Mercuric Compounds

22. Mercuric oxide, HgO, is slowly formed as a red powder when mercury is heated in air just below its boiling point. It is usually prepared by heating the nitrate or a mixture of the nitrate and mercury: $Hg(NO_3)_2 + Hg = 2HgO + 2NO_2$. The partial pressure of oxygen over mercuric oxide is 985 mm. at 500° C. The oxide precipitates upon the addition of a strong base to a solution of a mercuric salt. Precipitated in the cold, the color is yellow, but from hot solutions, the color is red. The difference in color seems to be merely a question of the state of subdivision of the solid, as the two forms appear to have the same crystal structure and very nearly the same energy content. The yellow is the more reactive and also the more finely divided. The hydroxide is unstable, but a hydrate, $HgO \cdot 3H_2O$, exists. The oxide is soluble in excess iodide due to the formation of the complex iodide: $HgO + 4I^- + H_2O = HgI_4^{--} + 2OH^-$. Its solubility is said to be increased in alkali, presumably due to weak acidic properties and the formation of HgO_2^{--}. Mercuric ion in solution is more highly hydrolyzed than is to be expected from the value for the solubility of the oxide, Table I. However, the value for the oxide electrode: $Hg + 2OH^- = HgO + H_2O + 2E^-$, -0.099 volt, indicates that the concentration of Hg^{++} in the solution is very small.

23. Mercuric chloride, $HgCl_2$, "bichloride of mercury" or "corrosive sublimate," may be made by heating mercury in an atmosphere of chlorine. The reaction is accompanied by green radiation. It is usually prepared, however, by subliming a mixture of mercuric sulfate and common salt. The chloride is moderately soluble in water, and the solubility is increased by excess chloride ion due to the formation of complex ions, probably $HgCl_4^{--}$. The salt in solution is but slightly ionized, even less than cadmium chloride, as is indicated by its low electrical

conductivity, and by the value of the chloride as an oxidizing agent: $Hg + 2Cl^- = HgCl_2 + 2E^-$, -0.45 volt. This value is 0.41 volt lower than the $Hg\text{-}Hg^{++}$ couple. The solution is only slightly hydrolyzed, but the addition of dilute alkali results in the formation of various basic chlorides, such as $HgCl_2 \cdot HgO$. The chloride is much used as an antiseptic and is highly poisonous. It forms a slightly soluble compound with albumen, and advantage is taken of this fact in administering egg white as an antidote. As a poison it acts partly through the destruction of kidney cells to such an extent that death results in about two weeks from the inability of the body to eliminate its waste products. The commercial preparation is usually mixed with sodium chloride to increase the rate of solution.

24. Mercuric fluoride is more soluble and much more hydrolyzed than the chloride. The **bromide** is sparingly soluble, and the **iodide** still less soluble. The iodide exists in two modifications, a scarlet form stable below 128°, and a yellow form stable above that temperature. The yellow iodide may be super-cooled below the transition temperature, but readily changes to the scarlet when touched. Mercuric iodide dissolves in excess iodide forming the very stable complex iodide, HgI_4^{--}. A solution of the potassium complex iodide is known as **Nesseler's reagent,** and is used in detecting small amounts of ammonia (see below).

25. Mercuric ammonia compounds exist in interesting variety, divisible into three types: (1) with ammonia of crystallization, such as $HgCl_2 \cdot 2NH_3$; (2) basic salts of the ammonia system, that is, they are formed from the negative ions of ammonia, NH_2^-, NH^{--} and N^{---}, similar to negative ions of water OH^- and O^{--}, the simplest being of the type $HgNH_2Cl$; (3) salts which are both ammonolyzed and hydrolyzed. Many complex salts of this latter type exist. The most important are derivatives of Millon's base, $OHHgNHHgOH$, or $Hg_2NOH \cdot H_2O$. The addition of ammonium hydroxide to mercuric chloride solution precipitates the ammonobasic chloride, $HgNH_2Cl$. With mercurous chloride, the same compound mixed with mercury is formed. Ammonia and mercuric nitrate solution form $Hg_2N \cdot NO_3$ and a number of other complex salts. Nessler's reagent (Par. 24) gives, with ammonia, a yellow precipitate, the iodide of Millon's base, $Hg_2NI \cdot H_2O$.

26. Mercuric Sulfide.—Crystalline mercuric sulfide is red,

both as found in nature, cinnabar, and as prepared by subliming together mercury and sulfur; but the sulfide precipitated from solution by hydrogen sulfide is black and amorphous. Mercuric sulfide is the least soluble of all the metal sulfides, and does not dissolve in hydrochloric or nitric acids. It is, however, soluble in aqua regia and in bromine water, due to the stability of the complex halides. Hot concentrated nitric acid converts it into the difficultly soluble white complex, $Hg(NO_3)_2 \cdot 2HgS$. The sulfide is somewhat soluble in a solution of an alkali sulfide but not in ammonium sulfide. The artificial red sulfide is used as a pigment under the name of vermilion.

27. Mercuric nitrate and **sulfate** are formed by the action of excess nitric and hot concentrated sulfuric acids upon the metal. Both are soluble, but are rather highly hydrolyzed, and precipitate as basic salts, such as $Hg(NO_3)_2 \cdot HgO$ and $HgSO_4 \cdot 2HgO$, unless excess acid is present. Normal mercuric carbonate does not exist, but **basic carbonates,** such as $HgCO_3 \cdot 2HgO$, may be precipitated. **Mercuric cyanide,** $Hg(CN)_2$, is soluble, but is even less ionized than the halides, and like them forms a complex ion, $Hg(CN)_4^{--}$. When heated, it decomposes into mercury and cyanogen: $Hg(CN)_2 = Hg + C_2N_2$. This complex gives the smallest concentration of mercuric ion of any of the mercuric compounds except the sulfide.

Mercuric fulminate, $Hg(OCN)_2$, is formed by the addition of alcohol to a hot solution of mercury in nitric acid. The dry precipitate explodes upon being struck, and is used extensively in percussion caps. **Mercuric thiocyanate,** $Hg(CNS)_2$, is slightly soluble. "Pharaoh's serpents" are prepared from this salt by making it into a paste with gum-water. When dried and ignited it burns and forms a voluminous ash which assumes serpentine forms.

28. Analytical.—Mercurous ion, like silver, gives a curdy, white precipitate with chloride but, unlike silver chloride, the precipitate blackens with ammonia (Par. 25). The insolubility of mercuric sulfide in nitric acid and in ammonium polysulfide serves to identify mercuric ion. The addition of stannous chloride to mercuric ion in small amounts gives a white precipitate of mercurous chloride, and in excess, a grey precipitate of mercury. With mercurous ion, stannous chloride in small amounts gives an immediate precipitate of mercury. A copper wire in either

mercurous or mercuric solutions becomes coated with a grey or silvery deposit of mercury.

Mercury may be precipitated and weighed quantitatively as the sulfide, or electrolytically as the metal on a platinum cathode. It is sometimes determined by heating the sample in a combustion tube and passing the vapors through a weighing tube containing gold leaf to absorb the mercury. Mercurous salts may be precipitated and weighed as the chloride. Mercurie salts are sometimes analyzed volumetrically by titration with iodide.

CHAPTER IX

SUBGROUP III. GALLIUM, INDIUM, AND THALLIUM

1. The elements of Subgroup III are extremely rare and of slight industrial importance. They form compounds in which they have a valence of + 3, and, in the case of thallium, compounds also with a valence of + 1. In spite of the higher positive charge on their ions, they do not show as great tendencies to form "coordination compounds" or complexes as do the elements of Subgroup II. The first electron is rather easily removed, and as a consequence, compounds of the elements give characteristic colors in hot Bunsen flames; in fact, all of the elements of this group were discovered (between 1860–1875) through spectroscopic means. The name thallium (from Latin thallus, a budding twig) refers to its green spectrum; and the name indium, to its indigo-blue spectral lines. Gallium was named in honor of France (Latin, Gallia).

The trivalent compounds are similar to those of aluminum; with the exception that the acid character of the hydroxides decreases with increasing size of the atoms, and the potential of the ions as oxidizing agents increases.

2. Occurrence.—The elements occur widely distributed, but only in minute quantities. Gallium is a common constituent of zinc, iron, aluminum, and chromium ores, but is seldom present in quantities as high as 0.01 per cent. In small amounts, it is a very common impurity in pig iron and in commercial aluminum. Indium is usually associated with zinc blende, and often with ores of tungsten and tin. Its principal source is zinc, in which it sometimes occurs to the extent of 0.1 per cent. Thallium is associated with the alkalies, and also with iron, zinc, lead, tellurium, and other elements. It is most commonly obtained from the flue dust of sulfuric acid works in which thalliferous pyrites is burnt.

3. Preparation of Metals.—The extraction of the metals is largely a problem of separating the small quantities of their compounds from other metallic constituents, and is, therefore,

best considered after a discussion of the properties of the various ions. The metals are easily obtained by reduction with zinc, or by electrolysis.

TABLE I

ATOMIC AND PHYSICAL PROPERTIES

Element	Gallium	Indium	Thallium
Symbol	Ga	In	Tl
Atomic weight	69.72	114.8	204.39
Atomic number	31	49	81
Isotopes	69,71	115	——
Distribution of electrons in quantum levels, 1st	2	2	2
2d	8	8	8
3d	18	18	18
4th	3	18	32
5th		3	18
6th			3
Ionization potential of gaseous atoms in volts	5.97	5.76	6.08
Radius of ion in crystals, cm. $\times 10^8$	0.62	0.81	0.95(ic) 1.15(ous)
Melting point ° C.	29.75	155	303.5
Boiling point ° C.	>1,600	>1,450	1,650
Density	5.91	7.3	11.85
Electrical resistivity, ohm/cm. $\times 10^6$	53 at 0°	9 at 20°	18.1 at 20°
Electrode potential, $M = M^{+++}_{(aq.)} + 3E^-$ volts	+0.5?	+0.38	−0.79
Principal spectral lines, wave lengths, cm. $\times 10^8$	4,172.2 4,033.2	4,511.55 4,101.95 3,256.22 3,039.46	3,519.37 3,775.89 5,350.70

4. The Metals.—Many of the properties of the metals have been summarized in Table I. **Gallium** is a hard, brittle, grey metal. It melts just above room temperature, and remains a silver white liquid of low vapour pressure through a temperature range of about 1500 degrees. The metal expands upon changing from liquid to solid. The liquid supercools readily and may be kept in the liquid state even at 0° C. A possible application is in the construction of high temperature thermometers using quartz tubes. **Indium** is a lustrous silver metal almost as soft as lead, and is both ductile and malleable. **Thallium** is bluish-white in color, easily cut with a knife, malleable, but of low tensile

strength. The metal exists in two crystalline modifications with a transition at 226° C. Like the other two metals, the liquid is stable over a very long range of temperature.

5. Reactions of the Metals.—Gallium is only superficially oxidized in air at red heat; indium is not appreciably oxidized in air at 25°, but burns with a blue flame when heated, forming In_2O_3; thallium oxidizes slowly at 25°, and rapidly at higher temperatures, forming both Tl_2O and Tl_2O_3. Gallium and indium dissolve fairly readily in hydrogen ion with the evolution of hydrogen gas and the formation of the trivalent ions; thallium dissolves forming thallous ion or thallous salts. They unite directly with the more electronegative elements, and are, of course, oxidized by even moderately strong oxidizing agents, as indicated by their oxidation-reduction potentials (Table I).

TABLE II

REACTIONS OF THE METALS

$4M + 3O_2 = 2M_2O_3$	Ga slowly. Tl also forms Tl_2O
$2M + 6H^+ = 2M^{+++} + 3H_2$	With Ga and In. Tl forms Tl^+
$2M + 2OH^- + 2H_2O = 2MO_2^- + 3H_2$	With Ga
$2M + 3X_2 = 2MX_3$	X denotes halogens. Tl also forms TlX
$2M + 3S = M_2S_3$	Analogous reactions with Se, Te, P, As.

6. Gallic Ion and Its Compounds.—Gallic ion is colorless and its salts with colorless negative ions are white. Gallic **oxide,** Ga_2O_3, resembles aluminum oxide. The **hydroxide,** $Ga(OH)_3$, is precipitated by alkali and ammonium hydroxides, and the precipitate is soluble in excess of the reagent, forming **gallates.** Gallic ion, like aluminum, in the presence of carbonate ion, is completely hydrolyzed, leading to the precipitation of the hydroxide. The **sulfates, nitrates,** and **halides** are soluble, but the solutions are highly hydrolyzed and precipitate basic salts upon boiling. A **dichloride,** $GaCl_2$, appears to be formed by heating the trichloride with excess of the metal. The salt evolves hydrogen in water and forms basic gallic chloride. Gallic ion readily forms **alums.** The **ferrocyanide** is insoluble, even in solutions strongly acid with hydrochloric acid. The white **sulfide,** Ga_2S_3, is not precipitated except in the presence of other sulfides, such as zinc, copper, or arsenic, and then only when the solution is alkaline or but slightly acid.

7. Analytical.—Gallium is precipitated with the iron aluminum

zinc group in qualitative analysis. It may be separated from the other elements of the group, except ferric iron, by converting to the chloride and extracting with an ether-hydrogen chloride solution. The iron may be removed by reduction to ferrous and repeating the ether separation. The commercial separation from the zinc, with which it is usually associated, may be effected by converting into the chlorides, and fractional precipitation by sodium carbonate. The gallium concentrates in the first precipitate. It is separated from indium by taking advantage of the greater solubility of gallium hydroxide in excess alkali. The separation from zinc and indium may also be accomplished by fractional electrolytic precipitation. Quantitatively gallium is precipitated with aqua ammonia, removing the excess ammonia by boiling, and is weighed as the sesquioxide.

8. Indic Ion and Compounds.—The trivalent ion, In^{+++}, is colorless; ammonia or alkali hydroxides precipitate it as the **hydroxide,** $In(OH)_3$. The hydroxide forms the **sesquioxide,** In_2O_3, upon heating, and upon strong ignition the oxide, In_3O_4. Heated to 300° in hydrogen, the oxide, In_2O_2, appears to be formed. The hydroxide is somewhat soluble in excess alkali hydroxide (but not in dilute ammonium hydroxide), forming **indate** ion, InO_2^-. The carbonate is but slightly soluble, and, unlike gallium, is but slightly hydrolyzed. It is soluble in excess ammonium carbonate, but not in excess sodium carbonate. The **nitrate, sulfate, alums,** and **halides** are soluble. The halides resemble the cadmium compounds in that they are weak salts. **Mono-** and **dihalides** are formed by heating the trichlorides with excess metal, but these lower halides are unstable in water solutions: $3In^+ = In^{+++} + 2In$, and $3In^{++} = 2In^{+++} + In$. Yellow indium **sulfide,** In_2S_3, is precipitated by hydrogen sulfide in the presence of very dilute acid. It is somewhat soluble in a very high concentration of sulfide ion. The **cyanide** is but slightly soluble in water, but dissolves in excess cyanide. The **ferrocyanide** and **chromate** are also but slightly soluble.

9. Analytical.—The separation of indium from indiferrous zinc, the principal source of the element, is usually accomplished by dissolving the metal in acid, and precipitating indium and iron by the addition of ammonium hydroxide. The indium is separated from the iron present by dissolving the hydroxides and precipitating indium sulfide in acetic acid solution by hydrogen sulfide.

In the systematic qualitative separation, indium, like gallium, is precipitated with the iron-aluminum-zinc group. It is similar to zirconium and titanium in that the hydroxide is not dissolved when boiled with NaOH and Na_2O_2, but differs in the precipitation of the sulfide from a fluoride solution by NH_4OH and $(NH_4)_2S$.

10. Equilibria between Thallous and Thallic Ions.—Thallic ion, Tl^{+++}, is a strong oxidizing agent (Table III), being reduced to thallous ion, Tl^+. Further reduction requires a fairly powerful reducing agent. The reaction, $Tl^{+++} + 2Tl = 3Tl^+$, takes place practically to completion. Hot water is decomposed by thallic ion: $Tl^{+++} + H_2O = Tl^+ + 2H^+ + \frac{1}{2}O_2$. Thallic compounds decompose in general, upon heating, with the formation of the thallous compound: e.g. $TlCl_3 = TlCl + Cl_2$, and $Tl_2S_3 = Tl_2S + 2S$.

TABLE III

OXIDATION-REDUCTION POTENTIALS OF THALLIUM

	Volts
$Tl + I^- = TlI + E^-$	0.77
$Tl = Tl^+ + E^-$	0.336
$Tl^+ = Tl^{+++} + 2E^-$	−1.2

11. Thallous Ion and Compounds.—In the solubilities of most of its salts, thallous ion resembles divalent lead ion; while in size and other physical properties, basic nature of the hydroxide, and lack of tendency to form complex ions, it resembles potassium. Thallous ion is like stannous and plumbus ions in having a pair of valence electrons left in the valence energy level. **Thallous oxide,** Tl_2O, readily absorbs water to form **thallous hydroxide,** TlOH. The latter is fairly soluble and is a strong base. The decomposition pressure of steam over the hydroxide, $2TlOH = Tl_2O + H_2O$, reaches one atmosphere at 139° C. The **chloride, bromide,** and **iodide** are but sparingly soluble, and the solubility is decreased by the presence of excess halide ion. However, the **cyanide** appears to be soluble in excess cyanide ion. **Thallous sulfide,** Tl_2S, is precipitated in neutral or alkaline solution. **Thallous carbonate** is fairly soluble. The **chromate,** normal **phosphate, chloroplatinate,** and **cobaltinitrite** are sparingly soluble.

12. Thallic Ion and Its Compounds.—Thallic ion resembles aluminum ion except that it is larger, and its **hydroxide** does not

possess acid properties. The hydroxide is extremely insoluble and the soluble thallic compounds such as **sulfate** and **nitrate** are highly hydrolyzed. Oxygen reacts with thallium just below red heat to form thallic oxide, Tl_2O_3; at higher temperatures mixed thallic and thallous oxides are formed. Chlorine, passed into a suspension of thallous chloride, produces **thallic chloride.** Upon evaporation, the hydrate, $TlCl_3 \cdot 3H_2O$, may be obtained, and in the presence of ammonia the ammoniate, $TlCl_3 \cdot 3NH_3$, separates. The trichloride forms complex ions with excess chloride, and a complex **thallous chlorthallate** exists, $TlTlCl_4$. The **bromide** is quite similar to the chloride, but the **iodide,** TlI_3, is probably thallous triiodide. The **sulfide,** Tl_2S_3, is very unstable, and forms thallous sulfide and sulfur.

13. Analytical.—Thallous chloride is soluble in hot water and not in ammonia, thus resembling lead chloride. The iodide is much less soluble than the chloride and is considered the most satisfactory test for thallous ion. It is but slightly soluble in thiosulfate. The extraction of thallium from the flue dust of sulfuric acid plants is based upon the slight solubility of the chloride, the non-precipitation of thallous carbonate by alkali carbonates, the precipitation of thallous sulfide by ammonium sulfide, and the reduction of the compounds to the metal by zinc. Quantitatively, thallium is usually precipitated and weighed as the thallous iodide. It may also be determined by titrating with standard permanganate, which in acid solution oxidizes thallous salts to thallic.

CHAPTER X

GROUP VII. THE HALOGENS: FLUORINE, CHLORINE, BROMINE, IODINE

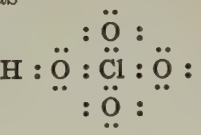
1. The elements of Group VII, fluorine, F, chlorine, Cl, bromine, Br, iodine, I, are called the halogens from a Greek word meaning salt-producing, since they all combine with the alkali metals to produce salts like sodium chloride. Fluorine and chlorine are gases; bromine is a volatile liquid; and iodine is a solid, easily melted and vaporized. The chemical behavior of these elements is related to the fact that each has 7 valence electrons in the highest energy level of its atoms (Table I). The removal of one of the 7 valence electrons requires a rather high potential, as shown by the value of the ionization potential of the gaseous atoms. This group tends to add an extra electron so as to produce the octet of the noble gas element of next higher atomic number (Chap. II). With increasing size of the atoms, i.e. going down the periodic group, the attraction for the electrons decreases, as is shown by the decreasing ionization potential and electron affinity. Due to their high electron affinity the halogens are powerful oxidizing agents, $X_2 + 2E^- = 2X^-$, although much of the energy of the reaction in water arises from the energy of hydration of the negative ion. Fluorine not only has the largest electron affinity, but, due likewise to its small size, the ion has the highest energy of hydration; consequently fluorine is the most powerful oxidizing agent the chemist can prepare.

These elements, with the exception of fluorine, also give compounds in which their valence may be considered positive, as illustrated by the following:

	$HClO$	$HClO_2$	$HClO_3$	$HClO_4$
Valence number.....	+1	+3	+5	+7

It is somewhat arbitrary to assume that the halogen has lost electrons to the oxygen in such compounds, for the electrons

are probably in reality shared by both, as indicated by the electron formulas, such as



where the only way to preserve the idea that the halogen is positive is to assume that the bonding pair of electrons are relatively more closely associated with the oxygen. Nevertheless, the assumption of positive valence numbers for the halogens in such compounds furnishes a useful basis for classification.

The tendency to form an octet with the valence electrons is made evident in the free element by the formation of the diatomic molecules in which the 2 atoms share their 7th electrons, so that each is in at least partial possession of an octet.

As might be expected, the bond grows weaker with increasing

TABLE I

PROPERTIES OF THE HALOGENS

Name	Fluorine	Chlorine	Bromine	Iodine
Symbol	F	Cl	Br	I
Melting point ° C	− 223	− 101.6	− 7.3	114
Boiling point ° C	− 187	− 34.6	58.8	184.3
Color of gas	Light yellow	Greenish yellow	Reddish brown	Violet
Atomic volume of solid, cc.	17.15	23.52	27.13	34.23
Atomic weight	19.0	35.46	79.92	126.92
Isotopes	None	35, 37	79, 81	None
Atomic number	9	17	35	53
Electrons in various quantum levels, 1st	2	2	2	2
2d	7	8	8	8
3d	—	7	18	18
4th	—	—	7	18
5th	—	—	—	7
Ionizing potential of gaseous atoms, volts	16.9	13.0	11.6	8
Electron affinity of gaseous atoms	—	3.9(?)	2.9(?)	2.6(?)
Radius of X^- in crystals, cm. $\times 10^8$	1.36	1.81	1.95	2.16
Heat of vaporization, cals. per mole	2,900	5,000	7,600	10,700
Heat of fusion, cals. per mole		1,634	2,380	4,500
Reaction $X_2 = 2X$: Heat, cals. per mole		60,000	42,000	35,000
Reaction $X_2 = 2X$: Dissoc. constant at 25°		10^{-18}	0.008	0.16
Dielectric constant of solid		2.0	3.2	4.0
Solubility in water, moles of X_2 per liter, 20°	Decomposes	0.090(1 atm.)	liq. 0.210	sol. 0.133
Distribution ratio, solubility CCl_4/H_2O, 0°	—	20.0	27.0	85.5

atomic radius, as shown by the increasing ease of dissociation, and also by the decreased constraint under which the shared electrons are held, which is evident from the increasing dielectric constant.

2. Occurrence.—The estimated per cent of the halogens in the earth's crust is: F, 0.1; Cl, 0.2; Br, 0.001; I, 0.001. Sea water contains about 2 per cent of chloride ion, and 0.006 per cent of bromide ion. The greater portion of the fluorine is in the form of fluorspar, CaF_2, and cryolite, Na_3AlF_3. The occurrence of great deposits of the alkali halides is discussed under the alkali elements. In addition to the alkali halides, there are found in nature chlorides, bromides, and iodides of the alkaline earths, silver, lead, copper, mercury, and bismuth. The major portion of the bromine of commerce is from the bromo-carnallite, $MgBr_2 \cdot KBr6H_2O$, of the Stassfurt (Germany) deposits, and from various American salt brines, especially those of the Saginaw Valley, Michigan. The principal source of iodine is the Chile deposits, where it occurs largely in the form of iodate, $NaIO_3$, and periodate, $NaIO_4$. Blood contains approximately 0.25 per cent chlorine as chloride ion, and the gastric juices 0.2 to 0.4 per cent free hydrochloric acid. Iodine is found in the various human tissues, the thyroid gland containing the highest per cent. Many marine plants exercise a selective absorption of iodide, even in the presence of far greater concentrations of chloride and bromide; hence dried seaweed is another important source of iodine.

3. Preparation and Uses of Free Elements.—**Fluorine** was first prepared by Moissan (1886) by the electrolysis of potassium fluoride in liquid hydrogen fluoride in a platinum vessel. It is now more conveniently prepared by the electrolysis of fused sodium or potassium hydrogen fluoride, using a copper vessel and graphite anode. Copper is attacked by fluorine, but the surface layer of copper fluoride protects the vessel from corrosion.

Chlorine. Although the greenish yellow fumes formed by the oxidation of chlorides by various oxidizing agents had long been observed, it remained for Scheele (1774) to clear up their meaning. He prepared chlorine by heating a mixture of manganese dioxide and hydrochloric acid. He considered the gas to be "dephlogisticated muriatic acid," meaning muriatic acid (hydrochloric) freed from phlogiston (the element of combustion).

Davy (1810) established its identity as an element. Scheele's method is still the one usually used for its laboratory preparation. It is also prepared by dropping dilute hydrochloric acid upon potassium permanganate: $2KMnO_4 + 16HCl = 8H_2O + 2KCl + 2MnCl_2 + 5Cl_2$, and by the action of dilute sulfuric acid upon bleaching powder: $CaCl(ClO) + H_2SO_4 = CaSO_4 + H_2O + Cl_2$.

Most of the chlorine of commerce is prepared by the electrolysis of brine as described under the preparation of sodium hydroxide. From the equilibrium electrode potentials (Append. II), one would expect oxygen to be liberated upon electrolysis of a brine solution; and this is the case in low concentration of salt: 0.2*N* NaCl yields about 20 per cent oxygen and 80 per cent chlorine at the anode. However, the oxygen evolution requires a high overvoltage (Append. I), and in more concentrated solutions only 1 or 2 per cent of oxygen is liberated.

The Deacon process, employing the oxidation of hydrogen chloride by oxygen (Par. 5), has been of some importance in the past. Attempts have also been made to operate the reaction, $MgCl_2 + \frac{1}{2}O_2 = MgO + Cl_2$, commercially at a high temperature. The magnesium oxide is reconverted to the chloride by hydrochloric acid.

Approxmately two thirds of the chlorine manufactured is used in bleaching, chiefly of pulp and paper. Large quantities are also used in water purification as a germicide, and in the manufacture of organic dyes, explosives, and chemicals. It is usually liquefied and sold in cylinders, or converted into bleaching powder, $CaCl(ClO)$, by action upon lime (Par. 5). The chlorine is again liberated from the bleaching powder upon the addition of acid. It was used extensively in the World War, at first directly as a poison gas, and later in the preparation of most of the other war gases, such as phosgene, $COCl_2$, and "mustard gas," $(C_2H_4Cl)_2S$. Some chlorine is converted into hydrogen chloride by burning in hydrogen, since the demand for electrolytic sodium hydroxide has often exceeded that for the chlorine formed as a by-product.

Bromine may be prepared from the bromides by any of the methods used for chlorine. It is recovered commercially in Germany from the waste liquors of the potash industry, and in America from various salt brines. The method depends upon the oxidation of bromide by chlorine. A commercial process

has been developed for the recovery of bromine from sea water. Free bromine is liberated by chlorine, and precipitated as tribromoaniline upon the addition of aniline. The process is capable of extracting a pound of bromine from 1,800 gallons of sea water.

Liquid bromine is used in the preparation of most of the bromides and other compounds of the element. Like chlorine, it is used in the preparation of intermediate products in the synthesis of organic compounds, an example being the lead-tetra-ethyl now added in small amounts to gasoline to prevent "knocking."

Iodine is extracted from kelp by oxidation of the iodides with chlorine, or manganese dioxide in acid, or even by sulfuric acid. The principal source is, however, the Chile deposits containing sodium iodate and periodate. Iodine is liberated by reduction with sodium bisulfite: $2IO_3^- + 5HSO_3^- = I_2 + 5SO_4^{--} + H_2O + 3H^+$; it is then removed and purified by sublimation.

Iodine is used in synthesis of aniline dyes, and iodides are employed somewhat in photography. It is also used in medicine as an antiseptic; in alcohol solution, known as tincture of iodine; in iodoform, CHI_3; and as metallic iodides, in the prevention and cure of goiter, and other disorders of the thyroid gland.

4. Physical Properties.—Table I gives the colors of the elements in the gaseous state. In the liquid state, the colors are, of course, deeper. Liquid bromine and iodine are opaque except in very thin layers. Solid iodine is dark grey with a slight luster.

Solutions of chlorine and bromine in water show colors closely resembling those of the gases. Iodine dissolves in many solvents, such as carbon tetrachloride, chloroform, and hexane, with a violet color resembling that of the vapor; but in solvents of high dielectric constant such as water and alcohol, its solution is brown. The progression in color in the gaseous halogens with increasing atomic weights is due to an absorption band, which in fluorine is nearly all in the ultra violet, removing only a little of the visible light at the violet end of the spectrum, thus causing the transmitted light to have an excess of the complementary color, yellow. With chlorine this band has moved down into the blue, and so on, until with iodine the band removes the middle portions of the visible spectrum allowing only red and violet light to be transmitted.

The density in the gaseous state corresponds to molecules of 2 atoms each, which is confirmed by the figures for the same elements in solution. Heated to sufficiently high temperatures, the diatomic molecules gradually break down into single atoms. The dissociation of iodine in this way becomes noticeable below 700°. Progressively higher temperatures would be necessary for the corresponding dissociation as we go from iodine to the lighter halogens, as indicated by the dissociation constants and heats of dissociation given in Table I.

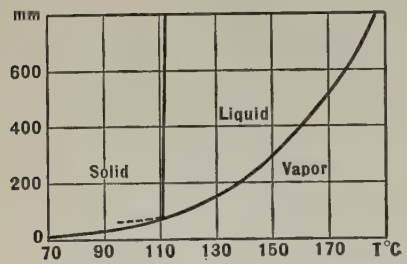


Fig. 1. Temperature-pressure diagram of iodine.

Although solid iodine may be melted at 1 atmosphere pressure, it sublimes without melting below a pressure of 100 mm. as is indicated in the phase diagram, Figure 1.

The halogens, with the exception of fluorine, are soluble in water (Table I). Chlorine and bromine form the hydrates, $Cl_2 \cdot 8H_2O$ and $Br_2 \cdot 10H_2O$. The former is stable up to 28.7° under a pressure of 6 atm. of chlorine, and the latter to 6.2° under a pressure of 93 mm. of bromine vapor. Above 28.7°, chlorine under pressure forms with water two liquid layers. Bromine likewise forms two liquid layers, but the lower layer contains only a very small amount of water, 0.04 per cent at 10°.

5. Reactions of the Halogens.—The chemical behavior as related to atomic structure, has been discussed in Paragraph 1. Fluorine and chlorine are capable of oxidizing all metals, while bromine and iodine can oxidize all but the noblest. The products of these reactions are halides. The halogens do not react directly with oxygen or nitrogen. Fluorine reacts directly with all other elements except nitrogen, oxygen, chlorine, and the noble gases; and chlorine with all but these and carbon. Bromine and iodine are less reactive.

The reactions of the halogens with hydrogen are discussed in detail under the hydrogen halides. The halogens act upon many hydrocarbons, displacing hydrogen and forming the halogen acid: e.g. $CH_4 + Cl_2 = CH_3Cl + HCl$. They also unite directly with many unsaturated compounds: $C_2H_4 + Cl_2$

$= C_2H_4Cl_2$ and $CO + Cl_2 = COCl_2$. They readily oxidize sulfur in most of its compounds: e.g. $CS_2 + 2Cl_2 = CCl_4 + 2S$.

The oxidation reduction potentials (Table II) of the free elements to the halide ions are extremely important, especially in connection with the general table (Append. II) in predicting many reactions. Thus, bromine will oxidize iodide, $I^- + \frac{1}{2}Br_2 = \frac{1}{2}I_2 + Br^-$, but will not oxidize chloride or fluoride; and all of the halogens except iodine will oxidize ferrous ion to ferric: $Fe^{++} = Fe^{+++} + E^-$, -0.74 volt.

TABLE II

OXIDATION-REDUCTION POTENTIALS OF HALOGEN-HALIDE COUPLES

	Volts$_{25°}$
$I^- = \frac{1}{2}I_2 + E^-$	-0.535
$Br^- = \frac{1}{2}Br_2 + E^-$	-1.065
$Cl^- = \frac{1}{2}Cl_2 + E^-$	-1.359
$F^- = \frac{1}{2}F_2 + E^-$	-2.8

The halogens undergo two important **reactions with water:**

$$(1)\ X_2 + H_2O = 2H^+ + 2X^- + \tfrac{1}{2}O_2$$
$$(2)\ X_2 + H_2O = H^+ + X^- + HXO$$

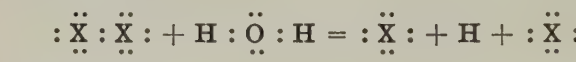
The potential values at 25° for reaction (1) in volts are: F_2, 2.0; Cl_2, 0.6; Br_2, 0.3, and I_2, -0.3 (i.e., in the reverse direction). Thus fluorine reacts vigorously with liquid water, liberating not only oxygen but ozone; chlorine reacts slowly in sunlight liberating oxygen. On the other hand, moist hydrogen chloride gas reacts with oxygen with the aid of a catalyst to give a detectable amount of chlorine. Bromine liberates oxygen only very slowly from water, and the reaction is reversed if the hydrobromic acid has a high concentration. Iodine, on the other hand, is liberated from a solution of hydrogen iodide by oxygen, the speed of the reaction increasing rapidly with an increase in hydrogen ion concentration.

At a temperature of 450°, an equilibrium is reached between chlorine, steam, hydrogen chloride, and oxygen by means of which it is possible to convert two-thirds of the hydrogen chloride into chlorine. This is the basis for the **Deacon process** once used for the manufacture of chlorine. Hydrogen bromide is completely oxidized to bromine at this temperature.

Reaction (2), the hydrolysis of the halogen, likewise takes

place less completely, the higher the atomic weight of the halogen. In the case of fluorine the reaction cannot be observed because of the rapidity of reaction (1). With the other halogens a reversible equilibrium is established. At 25°, the equilibrium constants are: for Cl_2, 4.8×10^{-4}; for Br_2, 5×10^{-9}; for I_2, 3×10^{-13}. The hydrolysis may in every case be largely repressed by the presence of acid, and increased by the addition of alkali. Thus, hydrogen chloride added to hypochlorite liberates chlorine; and chlorine in sodium hydroxide solution is converted completely into chloride and hypochlorite. For a $0.01M$ Cl_2 solution, the above equilibrium constant corresponds to about 85 per cent hydrolysis. The electronic picture of the hydrolysis consists of a splitting of the halogen molecule and a union of the positive halogen atom with water.

Electron formulas



Ordinary formulas

$$X_2 + H_2O = X^- + H^+ + XOH$$

TABLE III

SUMMARY OF IMPORTANT REACTIONS OF HALOGENS

X = halogen

$X_2 + H_2 = 2HX$	cf. Par. **7**
$X_2 + H_2O = 2HX + \frac{1}{2}O_2$	cf. Par. **5**
$X_2 + H_2O = H^+ + X^- + HXO$	cf. Par. **5**
$nX_2 + 2M = 2MX_n$	With most metals
$3X_2 + 2P = 2PX_3$	Also with As, Sb, Bi
$5X_2 + 2P = 2PX_5$	Not with I_2. Also As, Sb with F_2 and Cl_2
$X_2 + RH = RX + HX$	RH many organic hydrocarbons
$mX_2 + 2C_nH_m = 2mHX + 2nC$	At high temperature. Less readily with Br_2 and I_2
$X_2 + CO = COX_2$	With Cl_2 and Br_2
$X_2 + SO_2 = SO_2X_2$	With F_2 and Cl_2
$X_2 + H_2S = 2HX + S$	Excess H_2S
$X_2 + 2S = S_2X_2$	With Cl_2 and Br_2. F_2 forms SF_6, Cl_2 also forms SCl_4
$4X_2 + S_2O_3^{--} + 10\ OH^- = 2SO_4^{--} + 8X^- + 5H_2O$	
$I_2 + 2S_2O_3^{--} = S_4O_6^{--} + 2I^-$	Neutral or slightly acid solution
$3X_2 + 8NH_3 = 6NH_4X + N_2$	With F_2, Cl_2, Br_2
$3Cl_2 + NH_4^+ = NCl_3 + 4H^+ + 3Cl^-$	I_2 forms $NI_3 \cdot NH_3$ with NH_3
$2X_2 + TiO_2 + 2C = TiX_4 + 2CO$	With Cl_2 and Br_2. Also SiO_2, Cr_2O_3, etc.

Compounds of the Halogens

6. The Halogen Halides.—In view of the great difference in the electronegative character of the halogens, it is not surprising that the more positive form compounds with the more negative. Thus, iodine forms IF_5 (m.p. 10°), ICl (2 forms m.p. α 27.2°, β 13.9°), and IBr (m.p. 36°); and bromine forms BrF_3 (m.p. 4°). The positive character of the larger halogen in these compounds is indicated, for example, by electrolysis of liquid iodine chloride, ICl, and also by its solution in sulfur dioxide, whereby iodine is liberated at the cathode, and chlorine at the anode. Hydrolysis gives the corresponding oxy-acid of the positive halogen, and the halide ion of the other. $IF_5 + 3H_2O = IO_3^- + 5F^- + 6H^+$. Due to the instability of the lower oxy-acids, the first step is not always realized: thus, $5ICl + 3H_2O = 2I_2 + 5Cl^- + IO_3^- + 6H^+$.

Liquid chlorine and bromine mix in all proportions and there is no evidence of the formation of any compounds.

Iodine monochloride is formed by the direct action of chlorine upon iodine, and by the reaction, $HIO + HCl = ICl + H_2O$. Due to the latter reaction, iodine monochloride is often formed through the reduction of iodates, or the oxidation of iodides in concentrated hydrochloric acid. It hydrolyzes in dilute acid. If the formation of iodine monochloride in concentrated hydrochloric acid is accompanied by the liberation of chlorine, iodine trichloride, ICl_3, results.

7. Hydrogen Halides. Preparation.—The hydrogen halides may be formed by direct union of the elements. As shown in Table IV, the reaction: $X_2 + H_2 = 2HX$, decreases in energy with increasing atomic weight of the halogen. Fluorine and hydrogen combine instantly, even at a temperature of − 253° C., where fluorine is solid and hydrogen liquid. The rate of combination of hydrogen and chlorine is slow in the dark, but takes place with explosive violence in the sunlight, or at 250° C. The increased speed under these conditions is doubtless due to the absorption of radiant energy by the chlorine molecule, and the more rapid reaction of this activated molecule. Of course, as soon as a few molecules react, enough energy is liberated to activate many molecules. Some idea of the force holding the HCl molecules together is given by the consideration that the formation from hydrogen and chlorine involves the dissociation

of Cl_2, 60,000 cal., and H_2, 100,000 cal. The reactions of hydrogen with bromine and iodine are very slow at room temperature, and are catalyzed by light and by platinum at higher temperature.

TABLE IV

PROPERTIES OF HYDROGEN HALIDES

	HF	HCl	HBr	HI
Boiling point	19	− 85	−67	−36
Melting point	−83	−111	−86	−51
$H_2+X_2=2HX$ Heat kg. cal.	64.0	22.0	13.5	− 0.8
$H_2+X_2=2HX$ Per cent dissociation at 1000°		1.34×10^{-13}	0.144	29.0
Solubility in water 1 At. and 20° C. g. per 100 g. of solution	35.3	42	49	57
Heat of solution at infinite dilution, kg. cal.	11.6	17.3	19.9	19.2
Constant Boiling Mixture, 1 At. Temp.	120	110	126	127
Constant Boiling Mixture, 1 At. Density	1.14	1.10	1.49	1.70
Constant Boiling Mixture, 1 At. Wt. per cent of acid	35.37	20.24	47	57.0
Dielectric constant of liquid	—	9	6	3
Heat of neutralization of dilute acid in kg. cal.	16.2	13.4	13.4	13.4

Hydrogen fluoride and chloride are usually prepared by the action of the less volatile sulfuric acid upon a halide salt, such as CaF_2 and NaCl. In the case of hydrogen chloride, the reaction is the first step in the LeBlanc carbonate process (cf. **IV—13**). The acid sulfate is first formed: $NaCl + H_2SO_4 = HCl + NaHSO_4$, and the mixture is heated to a temperature of about 500°, in order to complete the second step: $NaCl + NaHSO_4 = HCl + Na_2SO_4$. Due to the oxidation of bromide and iodide by hot concentrated sulfuric acid, $H_2SO_4 + 2HI = I_2 + SO_2 + 2H_2O$, this acid is replaced usually by phosphoric acid in the preparation of hydrogen bromide and iodide. The acids may be prepared by the hydrolysis of the halides of the more negative elements, such as phosphorus, sulfur, or arsenic: $PBr_3 + 3H_2O = H_3PO_3 + 3HBr$. The halides of the noble metals may be reduced with hydrogen at a high temperature to form the hydrogen halide: $2AgCl + H_2 = 2Ag + 2HCl$. These acids are also formed by the action of the halogens upon many organic hydrocarbons: $C_6H_6 + Br_2 = C_6H_5Br + HBr$. A solu-

tion of hydrogen iodide is conveniently prepared by the action of hydrogen sulfide upon a suspension of iodine in water: $H_2S + I_2 = S + 2HI$.

8. Properties.—The hydrogen halides are all colorless gases; they possess a disagreeable pungent odor, fume strongly in moist air, are extremely soluble in water; their water solutions, with the exception of hydrogen fluoride, are strongly acidic. The water solutions are called hydrofluoric acid, hydrochloric acid, etc. In the pure liquid state, they have a low electrical conductivity, of about the same magnitude as that of pure water. The approximate values for the dielectric constants of the liquids indicate that the electrical polarization decreases with increasing molecular weight. Hydrogen fluoride gas polymerizes, forming $(HF)_6$. At 20° C. and 745 mm., 80 per cent of the HF is so polymerized. This property is not shown by the other gases.

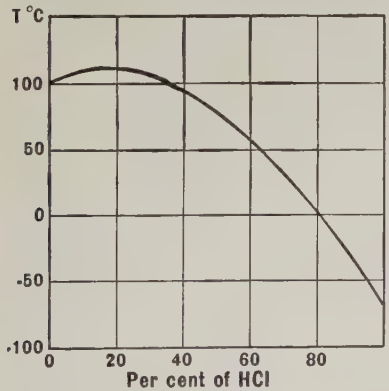


Fig. 2. Boiling point-composition curve for HCl.

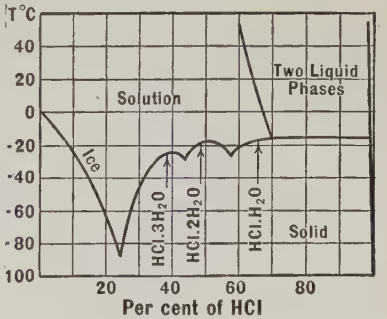


Fig. 3. The system water-hydrogen chloride.

The water solutions exhibit the phenomena of **boiling point maxima.** The temperature composition diagram for hydrochloric acid is given in Figure 2. The curve represents the temperature at which a given composition of the acid will boil, i.e. the temperature at which the sum of the pressures of hydrogen chloride and water equals atmospheric pressure. As a given solution boils, its composition changes toward that of the maximum boiling mixture. When this composition is reached, the solution boils without further change in composition. The composition of the maximum boiling mixture depends upon the total pressure.

For hydrogen chloride, 1 atmosphere, the value is 20.24 per cent HCl and the temperature 110°; for 2,500 mm., the composition is 18 per cent; and for 50 mm. it is 23.2 per cent. Advantage is often taken of these fixed concentrations to prepare acids of known concentrations for quantitative analysis.

Hydrogen chloride forms three definite hydrates, as indicated in Figure 3. The eutectic, − 86°, is remarkably low. Hydrogen bromide forms a di-, tri-, and tetrahydrate; and hydrogen iodide, tri-, and tetrahydrates.

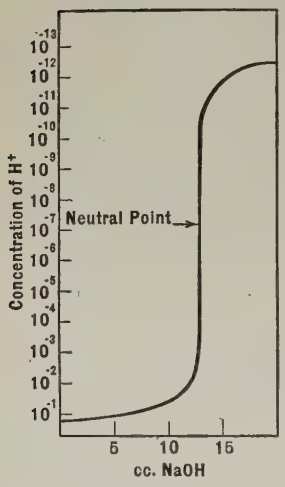


Fig. 4. Titration of HCl with NaOH.

The ionization of these acids in dilute solution is 100 per cent, as judged by the lowering of vapor pressure and freezing points, and by electrical conductivity. The apparent ionization at higher concentrations is discussed in Appendix IV. Hydrofluoric acid is much weaker than the other acids. In fairly concentrated solutions, it is largely polymerized to H_2F_2. Even in dilute solutions, its heat of neutralization is about 3 kg. cal. more than that of typically strong acids, which is unusual, as the heat of neutralization of other weak acids is less than that of strong acids. The change of concentration of hydrogen ion in hydrochloric acid, upon titration with hydroxide, is given in Figure 4.

9. Uses.—Hydrogen fluoride is used in etching glass. This remarkable property results from the action of hydrogen fluoride upon silicon dioxide: $SiO_2 + 2H_2F_2 = SiF_4 + 2H_2O$. The silicon fluoride escapes as a gas. Etched designs, such as burette graduations, are made by covering the glass with paraffin, which is scraped away where etching is desired, and then treating with a solution of the acid. A mixture of ammonium fluoride and hydrogen fluoride is used in frosting glass. The acid is also used in quantitative analysis, in dissolving complex silicates, since all silicates are decomposed through the removal of the silica. It has certain application in the curing of crude rubber, in cleaning the exterior of stone buildings, and in cleaning castings.

Hydrochloric acid is used in the preparation of metal chlorides, especially those of zinc and tin; in cleaning metal surfaces, particularly iron before galvanizing; and in the manufacture of glue, soap, glucose, dyes, and many other materials.

10. Halides and Halide Ions.—Fluoride. The fluorides of lithium, the alkaline earth, and the rare earth metals are sparingly soluble. Fluoride forms more stable complexes than do the other halides with small positive ions, for example, BF_4^-, SiF_6^{--}, AlF_6^{---}. These complexes are analogous to the corresponding oxygen acids, and their stability is doubtless due to high electrostatic attraction for the small fluoride ions. On the other hand, the fluoride ion is not as polarizable as the larger halides (cf. **VII—2**), and does not readily form coordination complexes with the ions of the noble metals.

The metal fluorides form acid salts of the type KHF_2, and even KH_3F_4, and the crystal structure of these compounds indicates that the hydrogen ion serves to bind two fluoride ions together:

$$:\ddot{\underset{\cdot\cdot}{F}}:H:\ddot{\underset{\cdot\cdot}{F}}:$$

11. Chloride. Among the most important sparingly soluble chlorides are those of Ag^+, Hg_2^{++}, Tl^+, Cu^+, Pb^{++}, Au^+, Pt^{++}, Pt^{++++}, SbO^+, and BiO^+.

The solubility of all metallic chlorides is decreased by a small excess of chloride ion, but a larger concentration often leads to an increase in solubility through the formation of complex ions. The alkali and alkaline earth elements do not form complex chlorides, but practically all of the subgroup and transition elements do: e.g. $MCuCl_2$, M_2ZnCl_4, M_3FeCl_6, M_3PtCl_6.

There is some evidence for the formation of trichloride Cl_3^- when chlorine is passed into concentrated hydrogen chloride (see Triiodide below).

Certain of the chlorides, especially the volatile chlorides of metals of higher valence, may be prepared by the action of chlorine upon a heated mixture of the oxide and carbon: e.g. $TiO_2 + 2Cl_2 + 2C = TiCl_4 + 2CO$.

Chlorides of the non-metals, e.g. CCl_4, PCl_5, SCl_4, are discussed under these elements.

Bromide. Bromide ion is very similar to chloride ion in the character of its slightly soluble compounds and complex ions, though in general the sparingly soluble bromides are somewhat less soluble than the corresponding chlorides.

Alkali bromides are usually prepared from bromine, by first forming ferrous bromide by action of bromine upon iron, and then carrying out the double decomposition with the alkali carbonate: e.g. $FeBr_2 + K_2CO_3 = FeCO_3 + 2KBr$.

Iodide. The iodide ion, being the largest and most easily polarized (cf. **VII—2**) of the halides, forms very insoluble salts, and very stable coordination complex ions with the subgroup metals. The stability of many of these compounds is limited, however, by the ease of oxidation of iodide to the free element. The method of formation of the alkali iodides is similar to that of the bromides, *vide supra.*

Iodide ion readily dissolves iodine with the formation of **triiodide**: $I^- + I_2 = I_3^-$, the constant $(I^-)(I_2)/(I_3^-) = 1.4 \times 10^{-3}$ at 25°. This reaction is important as a means of bringing iodine into aqueous solution. Higher polyiodides are formed in very concentrated solutions.

In neutral solution, iodide is not readily oxidized by oxygen in the air; but in acid solution, the reaction becomes rapid: $6I^- + O_2 + 4H^+ = 2I_3^- + 2H_2O$. The quantitative oxidation of iodide by powerful oxidizing agents, e.g. H_2O_2 or $KMnO_4$, is extremely important in quantitative analysis (Par. 21).

12. Oxygen Compounds of the Halogens.—Fluorine and bromine form no stable oxides, though there is some evidence for the formation of an unstable oxide of fluorine. Chlorine forms the oxides Cl_2O, ClO_2, and Cl_2O_7; and iodine, the oxides I_2O_4 and I_2O_5. A number of additional oxides as ClO_3, ClO_4, and I_2O_3 have been described, but they are extremely unstable. None of these oxides are formed by direct union of the elements. The oxides possessing an odd valence of the halogen are anhydrides of the corresponding acids. The oxygen acids of the halogens are given in the following summary.

TABLE V

Oxygen Acids of the Halogens

Valence	Name	Chlorine	Bromine	Iodine	Name of Ion
+1	hypo-ous	$HClO$	$HBrO$	HIO	hypo-ite
+3	-ous	$HClO_2$	$(HBrO_2)$	(HIO_2)	-ite
+5	-ic	$HClO_3$	$HBrO_3$	HIO_3	-ate
+7	per-ic	$HClO_4$	—	HIO_4 and H_5IO_6	per-ate

The halous acids and their salts are of the least importance. Indeed the existence of $HBrO_2$ and HIO_2 is but momentary, usually as an intermediate reaction step.

The halogen oxyacids are powerful oxidizing agents, as is indicated in the accompanying table, which gives the potential in volts for their reductions to the halide ions.

TABLE VI

OXIDATION-REDUCTION POTENTIALS OF HALOGEN ACIDS

$Volts_{25°}$

Couple	Cl	Br	I
$X^- + H_2O = H^+ + HXO + 2E^-$	− 1.50	− 1.33	− 0.99
$X^- + 3H_2O = 6H^+ + XO_3^- + 6E^-$	− 1.45	− 1.42	− 1.09
$X^- + 4H_2O = 8H^+ + XO_4^- + 8E^-$	− 1.35		− 1.4
$X^- + 2OH^- = XO^- + H_2O + 2E^-$	− 0.94		

Since the oxyacids of chlorine and bromine are sufficiently powerful oxidizing agents to liberate oxygen from water ($2H_2O = O_2 + 4H^+ + 4E^-$, − 1.23 volts), it follows that water solutions of these acids are unstable. These decompositions are slow, but are catalysed by certain substances.

It may also be observed from the table that the oxidizing potentials of the halates decrease with increasing atomic weight, so that iodine will replace bromine in bromate, and bromine will replace chlorine in chlorate: e.g. $2BrO_3^- + I_2 = 2IO_3^- + Br_2$. The reactions take place in highly acid solution, and while they are often called replacement reactions, they are in reality complicated oxidation-reduction reactions.

With the exception of perchloric acid, the potentials are greater than those of the halogens to halide; hence, these acids are reduced by the halide ion. $HClO + H^+ + Cl^- = Cl_2 + H_2O$; $IO_3^- + 6H^+ + 5I^- = 3I_2 + 3H_2O$.

The positive univalent state is unstable in regard to its own oxidation and reduction into halate and halide; thus $3XO^- = XO_3^- + 2X^-$, and in dilute acid: $3HXO = XO_3^- + 2X^- + 3H^+$. Due to the reduction of the oxygen acids by the halide as mentioned above, this reaction in high acid concentration approaches the stoichiometric equation: $5HXO = XO_3^- + H^+ + 2X_2 + 2H_2O$. The speed of decomposition increases

rapidly in order from hypochlorous to hypoiodous. In the case of chlorate ion, we encounter instability with respect to perchlorate and chloride ions, according to the equation: $4ClO_3^- = 3ClO_4^- + Cl^-$. This occurs readily in the fused state.

13. Chlorine Monoxide and Hypochlorite.—Chlorine monoxide, Cl_2O, is the anhydride of hypochlorous acid, HClO. Its reaction with water, $Cl_2O + H_2O = 2HClO$, is reversible. The gas, at 1 atmosphere and 0°, is in equilibrium with a solution containing about 200 volumes of the gas per volume of solution. It is most conveniently prepared by the action of chlorine upon finely divided mercuric oxide: $2HgO + 2Cl_2 = Cl_2O + Hg_2OCl_2$. The reaction is carried out at about 0°, at which temperature the gas condenses to a liquid. The gas and liquid have a deep yellowish red color, and are highly explosive.

The hydrolysis of chlorine (Par. 6) yields hydrochloric acid and hypochlorous acid. The equilibrium is displaced by hydroxide through the neutralization of these acids: $Cl_2 + 2OH^- = H_2O + Cl^- + ClO^-$. A solution containing chloride and hypochlorite is easily prepared by the electrolysis of a solution of NaCl in a cell permitting the chlorine produced at the anode to react with the OH^- produced at the cathode. This solution is a cheap, efficient, and widely used disinfectant and bleaching agent. For household use, it can be purchased under the name of "chlorox."

When chlorine is passed over slaked lime, a reaction occurs which is closely related to the one given above: $Cl_2 + Ca(OH)_2 = H_2O + CaCl(ClO)$. The two ions, Cl^- and ClO^-, here remain attached to the same calcium ion. The resulting compound is known as **"bleaching powder."** or **"chloride of lime."** Upon solution in water it gives the corresponding ions; hence, when an excess of acid is added, chlorine is liberated, corresponding to the shift of the hydrolysis equilibrium of chlorine. Bleaching powder is extensively used for bleaching and disinfecting. Any solution containing both Cl^- and ClO^- can be made to yield chlorine in almost any desired concentration by suitably fixing the hydrogen ion concentration. However small the equilibrium concentration of chlorine, it will nevertheless be approximately maintained as the chlorine is used up. Such a solution is much used in surgery under the name "Dakin's solution."

One equivalent of acid, acting upon bleaching powder, liberates the weak hypochlorous acid, HClO, which may be distilled from the solution and thus separated from chloride ion. The dissociation constant of the acid is 6.7×10^{-10}.

The familiar odor of bleaching powder is due to hypochlorous acid liberated by the carbonic acid of the air.

Hypochlorite solutions readily give off oxygen (Par. 5) in the presence of a catalyst, e.g. cobalt hydroxide. Heated in the absence of a catalyst, the following reaction occurs: $3ClO^- = ClO_3^- + 2Cl^-$. The rate is increased if the solution is slightly acid.

14. Chlorites and Chlorine Dioxide.—Although chlorine dioxide and the chlorites are of different valence, they are discussed together because of the formation of chlorite by the reaction of the oxide in alkaline solution: $2OH^- + 2ClO_2 = ClO_2^- + ClO_3^- + H_2O$. Chlorine dioxide is one of the few "odd molecules" :Ö : Cl : Ö:, i.e. possessing an odd number of electrons; and the mechanism of the above reaction may be considered to be the transfer of the odd electron from one molecule of the oxide to another, forming ClO_2^- and ClO_2^+. The latter adds a molecule of hydroxide to form $HClO_3$. Chlorous acid is unstable except in very dilute solutions, and its salts are also unstable, decomposing to give (*a*) oxygen and chloride, and (*b*) chlorate and chloride.

The formation of chlorine dioxide from chloric acid is mentioned below (Par. 16). It may also be prepared by the action of chloric acid upon oxalic acid: $2HClO_3 + H_2C_2O_4 = 2ClO_2 + 2CO_2 + 2H_2O$. Chlorine dioxide is a gas at ordinary temperatures, and, like most substances having "odd molecules," is colored, in this case a dark yellow, and moreover is extremely unstable.

15. Chloric Acid and Chlorates.—Chlorates are easily prepared by decomposition of the hypochlorite (Par. 12). The process may be carried out, either by passing chlorine into hot alkaline solution, or by the electrolysis of a hot chloride solution with agitation so as to bring the chlorine from the anode into contact with the hydroxide of the cathode. Chloric acid decomposes upon distillation, and cannot be prepared in the pure state. A solution may be obtained by treating a solution of barium chlorate with dilute sulfuric acid: $Ba^{++} + 2ClO_3^- + 2H^+$

$+ SO_4^{--} = BaSO_4 + 2H^+ + 2ClO_3^-$. It is a strong acid and is much less stable than its salts. In addition to the decomposition into perchlorate and chloride and into oxygen and chloride, it may decompose according to the equation: $4HClO_3 = 4ClO_2 + O_2 + 2H_2O$. If concentrated sulfuric acid is added to solid chlorate, the above reaction takes place, and usually the ClO_2 formed explodes with great violence.

Potassium chlorate is the most important salt of chloric acid. While readily soluble in hot water, its solubility is but 3.1 g. per 100 grams of water at 0°. Advantage is taken of this behavior in preparing potassium chlorate by adding potassium chloride to a hot solution containing chlorate ion made from calcium hydroxide and chlorine, and then cooling.

Potassium chlorate decomposes at moderate temperatures as follows: $2KClO_3 = 2KCl + 3O_2$. This reaction is catalyzed by manganese dioxide, and furnishes a convenient laboratory method for the preparation of oxygen. If carefully heated to avoid the evolution of oxygen, potassium chlorate may be converted into the perchlorate: $4KClO_3 = 3KClO_4 + KCl$.

The oxidizing power of potassium chlorate renders it useful in making matches and pyrotechnics. Explosive mixtures may be made, using potassium chlorate with combustible substances such as charcoal, sugar, or sulfur; they are too treacherous to be of practical value. A solution of potassium chlorate is sometimes used as a gargle in throat infections.

All of the chlorates are at least moderately soluble. **Lithium chlorate** is one of the most soluble of all salts, 100 g. of water dissolves 315 g. of the salt at 18°.

16. Perchloric Acid and Perchlorates.—As mentioned in the previous section, perchlorates may be prepared by carefully heating chlorates. They may also be prepared by anodic oxidation in the electrolysis of concentrated chlorate solutions: $ClO_3^- + H_2O = ClO_4^- + 2H^+ + 2E^-$. Although this half reaction only requires a calculated potential of about one volt, it is difficult to find an oxidizing agent capable of bringing it about, since the oxidizing agent must at the same time be more powerful than chlorate; persulfuric acid or sodium bismuthate may, however, be used for this purpose. Perchloric acid may be distilled from a solution formed by the addition of sulfuric acid to a perchlorate. The pure acid is a volatile liquid at

ordinary temperatures, and decomposes at 92° under atmospheric pressure. The acid reacts explosively with strong reducing agents. It combines with water to form the solid hydrate, $HClO_4 \cdot H_2O$, with the evolution of much heat. The addition of phosphorus pentoxide to perchloric acid, cooled below 0°, results in formation of **perchloric anhydride:** $6HClO_4 + P_2O_5 = 2H_3PO_4 + 3Cl_2O_7$. This oxide is a colorless liquid which may be heated to its boiling point, 82°, without decomposition. It is easily detonated, however, by a sudden shock.

The perchlorates are safer to handle than the chlorates. They are used in matches, fireworks, and explosives. They are as a rule readily soluble, potassium, rubidium, and cesium perchlorates being the least soluble. Due to its slight solubility, potassium perchlorate is easily prepared and purified. It is probably the most important of the salts.

If silver perchlorate is treated with bromine, silver bromide and **free perchlorate radical,** ClO_4, result: $2AgClO_4 + Br_2 = 2AgBr + ClO_4$. This substance also has an odd number of valence electrons, and is extremely reactive and unstable.

17. Hypobromite and Hypoiodite.—The hydrolysis of the halogens decreases markedly with increasing atomic weight (Par. 5); however, in strongly alkaline solution both bromine and iodine are almost completely converted into the halide and hypohalite. Hypobromous acid, and more especially hypoiodous acid are very unstable, decomposing almost immediately into the halide and halate. They are also extremely weak acids. In fact, the reaction, $IOH + HCl = ICl + H_2O$, indicates certain basic tendencies in the latter. Hypobromites and hypoiodites decompose much more readily than hypochlorites to give halate and halide.

18. Bromate and Iodate.—In addition to the methods of preparation analogous to the chlorine compounds, bromic and iodic acids may be prepared from the elements by the action of powerful oxidizing agents such as hypochlorous, chloric, and nitric acids, and hydrogen peroxide. Bromic acid cannot be prepared in the pure state, as the concentrated solutions decompose forming oxygen and bromine. The bromates are in general less soluble than the chlorates, and may be distinguished from the latter by the insolubility of silver bromate. They have some industrial applications as oxidizing agents.

Iodic acid is a deep colored solid very soluble in water. It is most conveniently prepared in a pure state by the action of a slight excess of chloric acid upon iodine, or by the action of hydrogen peroxide in acid solution upon iodine. It may be dehydrated by careful heating to form the **pentoxide,** I_2O_5. This is a white solid which may be heated to about 300° before decomposition becomes rapid. Sodium iodate, occurring in the Chile nitre beds, has been mentioned as the most important source of the element. The iodates are much less soluble and much more stable than the other halates, and are easily distinguished from them by the insolubility of their barium and lead salts. Iodates in acid solution do not oxidize chloride. Neither the acid nor the salts show any tendency to decompose to form the periodates. Potassium iodate and bi-iodate, $KH(IO_3)_2$, are of considerable importance in analytical chemistry (Par. **21**), because of the quantitative reduction to iodine in dilute acid and to iodine chloride in concentrated hydrochloric acid by many reducing agents.

19. Iodine Tetroxide.—The oxide, I_2O_4, may be prepared by the action of concentrated sulfuric acid upon iodic acid, similar to the preparation of chlorine dioxide. It reacts with water according to the equation: $5I_2O_4 + 4H_2O = 8HIO_3 + I_2$. With sulfuric acid, it forms a complex compound, $(IO_2)H_2SO_4$.

20. Periodic Acid and Periodates.—Strong oxidizing agents convert the iodates into periodates. There is a long series of polybasic periodic acids which may be considered as derived from the anhydride, I_2O_7, by the addition of n molecules of water, $I_2O_7 \cdot nH_2O$, where n has the values 1 to 7: e.g. $I_2O_7 + H_2O = 2HIO_4$; $I_2O_7 + 2H_2O = H_4I_2O_9$; $I_2O_7 + 7H_2O = 2H_7IO_7$. The existence of H_7IO_7, or its salts, is somewhat doubtful, but salts of the acid, H_5IO_6, are the most common type. The higher polybasic acids may be dehydrated to form the meta acid, HIO_4; but the anhydride, I_2O_7, cannot be prepared as further heating causes decomposition into oxygen and the pentoxide. The fact that the iodine atom in periodic acid is surrounded by as many as six oxygen atoms, while the chlorine atom in perchloric acid is limited to four may be correlated with the larger size of the iodine atom.

The preparation of periodates is usually accomplished by heating iodate with chlorine in alkaline solution: $2Na^+ + IO_3^-$

$+ 3OH^- + Cl_2 = Na_2H_3IO_6 + 2Cl^-$. The product, disodium paraperiodate, is but moderately soluble. In highly acid solution the periodates are extremely powerful oxidizing agents, being capable of oxidizing manganous ion to permanganate, which requires a potential of $-$ 1.5 volts. Excess periodate, in even low acid concentration, is reduced to iodate by iodide: $2H^+ + IO_4^- + 2I^- = IO_3^- + I_2 + H_2O$. With excess iodide, the product is triodide.

21. Analytical Properties.—Advantage is taken of the insolubility of silver chloride, bromide, and iodide in both the qualitative and quantitative determination of these halides (cf. **VII—27**). Iodides and bromides are readily distinguished from chlorides by the liberation of bromine or iodine by chlorine water, and the production of the characteristic colors upon extraction of the free halogen with carbon disulfide.

The oxygen compounds of the halogens may be determined qualitatively by the reduction to the free element or halide, and identified as such. Quantitatively they may be reduced by excess reducing agent, such as stannous chloride, or titanous chloride, and the excess reducing agent titrated with permanganate; or they may be reduced with excess iodide and the iodine formed titrated with thiosulfate: $I_3^- + 2S_2O_3^{--} = 3I^- + S_4O_6^{--}$.

The reaction just given for the oxidation of thiosulfate by iodine or triodide is one of the most important in chemical analysis. Not only may it be employed in the determination of oxidizing agents, as indicated above, by the addition of excess iodide and the titration of the iodine by thiosulfate, but it may also be used to determine reducing agents by adding excess iodate and again titrating the iodine formed by thiosulfate. As an end point indicator in this titration, soluble starch is added to the solution, giving a deep blue color as long as an appreciable concentration of iodine is present.

CHAPTER XI

GROUP V. N, P, As, Sb, Bi

1. The elements of Group V, nitrogen, phosphorus, arsenic, antimony, and bismuth, have a maximum positive valence number of five in agreement with the presence of five valence electrons. The nitrogen atom, the smallest of the group, shows strong tendencies to add three additional electrons and thus complete the octet; but this property decreases with increasing size so that bismuth forms no stable compounds in which it has a negative valence number. Nitrogen and phosphorus are non-metallic in their properties, but the heavier elements of the group are increasingly metallic. Each of the elements forms an acid pentoxide, though the acidic nature of the oxide decreases markedly with increasing size of the positive ions. The elements also form sesquioxides which are acidic with the lighter members, but become basic with the heavier. The elements of the group thus show a complete transition from non-metallic to metallic character.

Nitrogen, like the first member of other groups, differs in many respects from the other elements. For this reason, and also because its importance warrants a more detailed treatment, it will be considered separately. A further discussion of the group properties is given in Paragraph **40.**

NITROGEN

2. Occurrence.—Four-fifths by volume of the atmosphere is free nitrogen, N_2. All fertile soils contain the element in the form of ammonium salts, nitrates, or nitrites; and nitrogen is a constituent of all proteins. The occurrence of deposits of alkali nitrates has been mentioned (cf. **IV—23**). The amount of nitrogen in the primary rocks is so small that nitrogen ranks among the less abundant elements, constituting but 0.03 per cent of the earth's crust and atmosphere.

3. Preparation.—Atmospheric nitrogen is the cheapest source of the element, and large quantities are prepared commercially from the air by fractional liquefaction (cf. **III—6**). This process

concentrates the argon somewhat (to about 3 per cent), but the gas is sufficiently pure for most commercial purposes. Nitrogen may, of course, be prepared from the air by the absorption of oxygen by chemical agents, such as heated copper. Pure nitrogen is usually prepared, either by passing ammonia over copper oxide: $2NH_3 + 3CuO = N_2 + 3H_2O + 3Cu$, or by heating a solution containing ammonium and nitrite ions: $NH_4^+ + NO_2^- = N_2 + 2H_2O$. Once the latter reaction is started, it proceeds rapidly or even explosively unless cooled. Other reactions producing nitrogen under appropriate experimental conditions are: $MnO_2 + 4NH_4NO_3 = Mn(NO_3)_2 + 8H_2O + 3N_2$; $(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2$; $2P + 5NH_4NO_3 = 2H_3PO_4 + 7H_2O + 5N_2$; $CO(NH_2)_2 + 2HNO_2 = CO_2 + N_2 + 3H_2O$.

4. Properties of Molecular Nitrogen.—The more important physical properties of atomic and molecular nitrogen are summarized in Table I.

TABLE I

PHYSICAL AND ATOMIC PROPERTIES OF NITROGEN

Atomic weight	14.008	Melting Point, ° C.	−209.8
Atomic number	7	Boiling Point, ° C.	−195.8
Isotopes	None	Density of liquid, g./cc.	0.808
Electrons in various quantum levels, 1st	2	Heat of vaporization cal. per mole	1350
2d	5	Solubility of N_2 at 1 atm. in g. per 100 g.	
Ionization potentials of gaseous atom, volts	14.5 and 21.9	water, 20° C.	0.00189
		100° C.	0.00069
Ionization potential of molecule, volts	16.5	Density of gas at 0° C. and 1 atm., g./liter	1.2506
Radius of M^{-3} ion, cm. $\times 10^8$ (if $Cl^- = 1.81$)	1.71	Heat of dissociation of N_2 in kg. cal. per mole	274

The gas is colorless and tasteless. The low boiling point is indicative of the stability of the molecule. Although the arrangement of the 10 valence electrons in the molecule is not known, the symmetrical formula

$$:\dot{N}:\dot{N}:$$

seems the most probable. The molecule is diamagnetic. The heat of dissociation is probably greater than that of any other

diatomic molecule, and is doubtless the chief factor in its very slight reactivity. It may be calculated from thermal data, that at 8000° C., the gas is only about 40 per cent dissociated into atomic nitrogen. Under the influence of a high voltage discharge, i.e. high velocity electrons, the nitrogen molecule is "activated." Active nitrogen appears to be atomic nitrogen, in which one or more electrons are raised to higher energy levels. Active nitrogen continues to glow for some time after the discharge has been stopped. It combines readily with many elements, phosphorus, sulfur, sodium, etc., with which ordinary nitrogen does not react. The nitrogen atom appears to have two ionization potentials, indicating that the five valence electrons do not all have the same energy.

The more important reactions of the element are given in Table II and will be discussed further in connection with the various compounds.

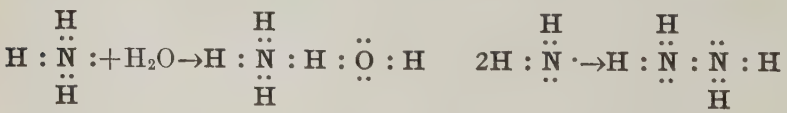
TABLE II

Reactions of Nitrogen

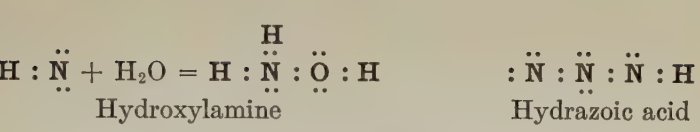
$N_2 + 3H_2 = 2NH_3$	See ammonia
$N_2 + O_2 = 2NO$	See nitric acid
$N_2 + CaC_2 = CaCN_2 + C$	See cyanamide process
$N_2 + 3Mg = Mg_3N_2$	Also Li_3N, Ca_3N_2, BN, AlN, TiN, etc.
$N_2 + Al_2O_3 + 3C = 2AlN + 3CO$	
$N_2 + 4C + Na_2CO_3 = 2NaCN + 3CO$	See also **XIII—24**

Compounds of Nitrogen and Hydrogen

5. Nitrogen forms with hydrogen compounds of polar valence number, -3, -2, -1, and a trinitride with an average polar number of $-1/3$. The most important of these are the -3 compounds, ammonia and its derivatives. The compound, NH_2, exists only in the double molecule, N_2H_4, hydrazine, and the compound NH is known only as the hydrate, NH_2OH, hydroxylamine, and its derivatives. The probable electronic structures of these compounds are given below:



Ammonia — Ammonium hydroxide — Hydrazine



Hydroxylamine Hydrazoic acid

6. Manufacture of Ammonia.—Ammonia was formerly made by the destructive distillation, in the absence of air, of hoofs, horns, and other nitrogenous organic substances; and the solution of the gas was called "spirits of hartshorn." Coal, due to its vegetable origin, contains nitrogenous matter, and one of the chief sources of ammonia has been the **" by-product ammonia,"** from coke ovens and coal gas works, in which ammonia produced by the distillation of the coal is separated from the other coal-tar products. The gas is usually washed with water to separate it from the tar, then with sulfuric acid which removes the ammonia as ammonium sulfate. Pure ammonia may be prepared from this by evaporation and treatment with calcium hydroxide.

7. One of the most important industrial developments of recent years has been the **production of synthetic ammonia** through the direct reaction of hydrogen and nitrogen: $3H_2 + N_2 = 2NH_3$. The reaction evolves 24,000 cal.; hence, the formation of ammonia is favored by low temperatures, and due to the volume change, by high pressure (cf. Principle of Chatelier, Hildebrand, *Princ. of Chem.*, p. 221), as is indicated in the following table.

TABLE III

VOLUME PER CENT AMMONIA IN EQUILIBRIUM WITH A 1 TO 3 MOLAL MIXTURE OF N_2 AND H_2

t ° C.	Atmospheres				
	30	100	300	600	7000
200	67.6	81.5	90.0	95.4	98.3
300	30.3	52.0	71.0	84.2	92.5
400	10.2	25.1	47.0	65.2	79.9
500	3.5	10.6	26.4	42.1	57.5
600	1.4	4.2	13.8	23.1	31.4
700	0.7	2.2	7.3	12.6	12.9

The rate of reaction is slow at the lower temperatures, and the commercial process has been dependent upon the development of efficient catalysts. The Haber process, developed in Germany,

employed according to the original patents, iron oxide containing other metals, such as molybdenum, uranium, or cobalt. Recently developed plants employ, as a catalyst, iron made by the reduction of fused iron oxide (magnetite) containing small amounts of both basic and acidic oxides, such as 0.5 per cent Al_2O_3 and 0.5 per cent K_2O; and operate at pressures of 100–200 atmospheres and temperatures of 550–600° C. The French Claude process attempts to utilize the greater yields at higher pressures by working at 600–1,000 atmospheres. Under these conditions, ordinary sheet iron is very permeable to hydrogen, and the containers must be constructed of special chrome-steel alloys. The world production of synthetic ammonia, in 1926, was over 500,000 tons.

8. Another source of ammonia is **calcium cyanamide,** $CaCN_2$, which is formed by the action of nitrogen upon calcium carbide (Table II) at about 1200°. When treated with steam, cyanamide is hydrolyzed: $CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$. Much of the cyanamide is used directly as fertilizer. Many of cyanamide plants are now being converted to the Haber process.

9. Attempts have been made to manufacture ammonia commercially by the hydrolysis of aluminum nitride in hot sodium hydroxide solution: $AlN + 3H_2O = Al(OH)_3 + NH_3$. The nitride is made by heating aluminum oxide and carbon in an atmosphere of nitrogen to about 1700°. The reaction is slow, and the process appears unable to compete with the direct synthesis from the elements. Ammonia may also be prepared by the hydrolysis of sodium cyanide: $NaCN + 2H_2O = HCOONa + NH_3$.

The historical laboratory method for the preparation of ammonia has been the reaction between an ammonium salt and a strong base (usually calcium hydroxide): $NH_4^+ + OH^- = NH_3 + H_2O$.

10. Physical Properties and Uses of Ammonia.—Ammonia boils at − 33.4°, melts at − 78°, has a critical temperature of about 133°, and a critical pressure of 112 atm. The vapor pressure of the liquid at 25° is 9.90 atmospheres, hence it is easily liquefied by pressure at that temperature. If the pressure upon the liquid is decreased to one atmosphere, the temperature of the liquid, of course, falls to − 33.4°, and the liquid evaporates with the absorption of 330 cal. per g. of ammonia vaporized.

This cycle of compression and evaporation is utilized in refrigeration.

The liquid has a density of 0.677 at $-34°$, and a dielectric constant of about 20. The specific conductivity at $-33°$ is about 10^{-8} reciprocal ohms. As a solvent for polar salts, it resembles water more closely than any other substance, although, due to the lower dielectric constant, salt solutions have a much lower activity (Append. IV). Its unusual solvent action upon the alkali metals has been mentioned (cf. **IV—2**).

Liquid ammonia is sold under pressure in iron cylinders, and is the most convenient source of the gas. The greater part of the ammonia produced is absorbed in sulfuric acid and sold as fertilizer. Household ammonia, or aqua ammonia, is used in washing and cleaning. Large quantities of ammonia are now oxidized to nitric acid (Par. **32**). The most important fields of consumption are given in Table IV.

TABLE IV

AMMONIA IN U. S. 1926

	Tons of N_2
Production	
Coke ovens	140,000
Synthetic	12,000
Gas works	5,000
Consumption	
Fertilizer (as ammonium salts)	57,000
Aqua ammonia	25,000
Liquid, largely for refrigeration	15,000
Explosives	8,000
Salts	5,000

11. Reactions of Ammonia.—Ammonia does not react readily with air, but in pure oxygen it burns to water and nitrogen: $4NH_3 + 3O_2 = 2N_2 + 6H_2O$; 301 kg. cal. In the presence of platinum as a catalyst, the reaction goes to nitric oxide: $4NH_3 + 5O_2 = 4NO + 6H_2O$, 215 kg. cal. This selective oxidation is the basis for the commercial preparation of nitric acid from ammonia (Par. **32**). The gas is also oxidized to nitrogen by passing over many heated oxides, e.g. CuO, and by chlorine and bromine (Par. **22**). The oxidation of ammonia and ammonium ion in water solutions is discussed in subsequent paragraphs.

Ammonia reacts with water to form ammonium hydroxide

(Par. 13). It is absorbed by many salts with the formation of ammoniated compounds similar to solid hydrates, e.g. $CaCl_2 \cdot 2NH_3$, $CaCl_2 \cdot 4NH_3$. Ammonia forms complex ions with solutions of many metal ions which possess pronounced "coordination" tendencies (cf. **VII—2**), e.g. $Ag(NH_3)_2^+$, $Cu(NH_3)_4^{++}$.

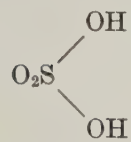
Ammonia shows acid properties, in that the three hydrogens are replaceable by metals as illustrated by the following: $NaNH_2$, sodium amide; Ag_2NH, silver imide; Li_3N, lithium nitride. These compounds are formed by heating the metals in ammonia gas: $2Na + 2NH_3 = 2NaNH_2 + H_2$. The acid ionization of ammonia, however, is extremely small, and even sodium amide is completely hydrolyzed in water: $NaNH_2 + 2H_2O = Na^+ + OH^- + NH_4OH$. The amides may be considered as the analogues of the hydroxides of water systems (Table V).

TABLE V

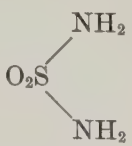
Analogy of Water and Ammonia Systems

	Water System	Ammonia System
First ionization step	H^+ and OH^- or H_3O^- and OH^-	H^+ and NH_2^- or NH_4^+ and NH_2^-
Ionization constant	10^{-14} at 25°	ca. 10^{-16} at $-33°$
Base	KOH	KNH_2
Acid	HCl (OH_3Cl)	NH_4Cl
Neutralization reaction	$KOH + (H_3O)Cl = KCl + 2H_2O$	$KNH_2 + NH_4Cl = KCl + 2NH_3$
Dehydration or deammoniation products of base	K_2O	K_2HN and K_3N
Basic salts	Mg(OH)Cl	$Hg(NH_2)Cl$
Solvates	$CaCl_2 \cdot 2H_2O$	$CaCl_2 \cdot 2NH_3$

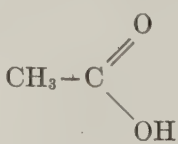
12. Many amino acids exist, both inorganic and organic, which may be thought of as formed by the replacement of the OH^- by NH_2^- (called amino in acids), e.g.,



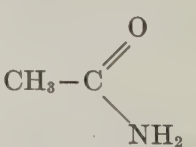
Sulfuric acid



Diaminosulfuric acid

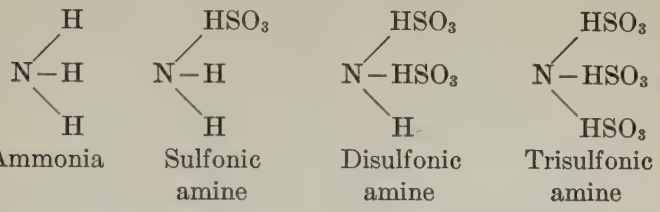


Acetic acid

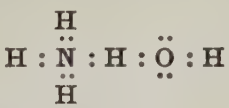


Aminoacetic acid

On the other hand, such acids may be considered as compounds in which one or more of the hydrogen atoms of ammonia is replaced by an acid radical, e.g.



13. Ammonium Hydroxide.—Ammonia is extremely soluble in water (1,300 vol. per vol. of H_2O at 0° and 700 vol. at 20°), forming solutions of ammonium hydroxide, NH_4OH. The hydroxide is a weak base: $NH_4OH = NH_4^+ + OH^-$, $K_{25°} = 18.1 \times 10^{-6}$. A 1*N* solution thus contains 0.0042*N* OH^-. To account for the weakness of ammonium hydroxide, it is generally assumed that a hydrogen atom acts as a bond as indicated by the formula:



Values for the specific gravity of aqueous solutions of ammonia are given in Table VI.

TABLE VI

SPECIFIC GRAVITY OF AQUEOUS AMMONIA AT 15° C.

Specific Gravity	Per Cent Ammonia	Specific Gravity	Per Cent Ammonia
0.998	0.45	0.940	15.63
0.994	1.37	0.930	18.64
0.990	2.31	0.920	21.75
0.980	4.80	0.910	24.99
0.970	7.31	0.900	28.33
0.960	9.91	0.890	31.75
0.950	12.72	0.882	34.95

Water and ammonia react to form solid ammonium hydroxide and the oxide, $(NH_4)_2O$, at $-79°$. These pure compounds decompose upon heating, so only the water solutions of ammonium hydroxide are known at room temperature.

14. Ammonium Amalgam.—The free ammonium radical, NH_4, may be prepared as an amalgam by the reduction of ammonium ion in the presence of mercury: $NH_4^+ + E^- = NH_4$. The reduction may be accomplished electrolytically, using a solution of ammonium sulfate and a mercury cathode, or by the action of sodium amalgam upon an ammonium solution. At ordinary temperature, the radical is unstable, decomposing into ammonia and hydrogen, and the amalgam is a spongy mass, due to the bubbles of gas, but at low temperatures the amalgam is a hard, stable substance. In forming an amalgam, the ammonium radical thus appears to possess distinctly metallic properties.

15. Ammonium Salts.—Ammonium ion resembles thallous and potassium ions in the solubility and crystalline form of its salts. The four hydrogen atoms are arranged in tetrahedral form about the nitrogen, and the approximate diameter of the ion in crystals is 1.50×10^{-8} cm. Two points of dissimilarity from thallous and potassium ions are the weakness of ammonium hydroxide, and the volatility of ammonium salts. All ammonium salts volatilize at temperatures around 300°, except compounds, such as the nitrate and dichromate, which decompose with the oxidation of the ammonia. The vapor of the sublimed salt is largely dissociated into ammonia and the acid, e.g. NH_4Cl (s) = NH_3 (gas) + HCl (gas). In fact, it is this dissociation taking place on the crystal surface which is probably responsible for the ready volatility of the salt. Ammonium salts are highly ionized, and slightly acid by hydrolysis. The constant for the hydrolysis, $K = (NH_4OH)(H^+)/(NH_4^+)$, is 5.5×10^{-9} at 25° C. A $1N$ NH_4^+ solution thus contains $7.4 \times 10^{-5}N$ H^+.

16. Ammonium chloride is made by absorbing ammonia in hydrochloric acid. It crystallizes from solution in feathery crystals of the regular system, having the same type of crystal lattice as cesium chloride, but changing at higher temperatures into the sodium chloride lattice. The vapor pressure of the solid reaches one atmosphere at 338° C. The salt is used in "galvanizing" iron, and in soldering, to clean metal surfaces of oxides, the action being due to the presence of free hydrochloric acid in the vapor. It is also used in "dry" batteries (cf. **XVIII—9**), and in textile dyeing. Its common name is sal ammoniac.

Ammonium bromide and **iodide** are similar to the chloride.

The **nitrate** exists in five crystalline modifications between the temperatures of $-20°$ and $125°$. When heated gently, it decomposes into nitrous oxide and water. The compound is really a high explosive, but is extremely difficult to detonate. It is, however, employed extensively as an explosive mixed with trinitrotoluene under the name of amatol.

17. Ammonium carbonate solutions are highly hydrolyzed, and lose ammonia to form the bicarbonate: $2NH_4^+ + CO_3^{--} = NH_4^+ + HCO_3^- + NH_3$. The so-called solid ammonium carbonate is a mixture of the bicarbonate and **ammonium carbamate,** and is made by heating a mixture of the ammonium sulfate and calcium carbonate in iron retorts. It may also be formed by the reaction of ammonia and carbon dioxide.

$$2NH_3 + CO_2 = \begin{matrix} & NH_2 \\ & / \\ C & = O \\ & \backslash \\ & O-NH_4 \end{matrix} \qquad \text{or} \qquad \left[\begin{matrix} & & :\ddot{O}: & & \\ & & \vdots & & \\ H : & \ddot{N} & : C : & \ddot{O} & : \\ & \vdots & & & \\ & H & & & \end{matrix} \right] NH_4$$

Upon heating, ammonium carbamate loses water to form **urea:** $NH_4CO_2NH_2 = CO(NH_2)_2 + H_2O$.

Ammonium sulfate, prepared by passing "by-product" ammonia into sulfuric acid, has been the principal source of ammonium compounds. Synthetic ammonia has, however, now become the greatest potential source of ammonium compounds. The sulfate is employed extensively as a fertilizer, but if a cheaper method of preparing phosphoric acid from phosphate rock can be developed, the sulfate will doubtless be replaced by the **phosphate,** as the absorption of ammonia in this acid will serve to eliminate the cost of the sulfuric acid and at the same time give a compound, both constituents of which are valuable fertilizers.

Ammonium sulfide, $(NH_4)_2S$, solutions, made by passing hydrogen sulfide into ammonium hydroxide, are largely hydrolyzed to the bisulfide, NH_4HS. The use of these solutions is frequently referred to in connection with the precipitation of metal sulfides in qualitative analyses. The sulfide readily absorbs sulfur forming polysulfides (cf. **XI—26**). The polysulfide also forms through the action of the oxygen of the air upon solutions of the sulfide.

Ammonium thiocyanate, NH_4CNS, is used in dyeing to prevent injurious action of iron salts upon the color (see $Fe(CNS)_3$). It is sometimes prepared by the reaction of ammonia and carbon disulfide: $CS_2 + 2NH_3 = NH_4CNS + H_2S$. Ammonium **dithiocarbamate,** $NH_4S_2CNH_2$, forms as an intermediate compound.

Ammonium peroxysulfate, $(NH_4)_2S_2O_8$, formed by the electrolysis of a concentrated solution of the acid sulfate, is an important oxidizing agent.

18. Analytical.—The perchlorate, cobaltinitrite, chloroplatinate, and acid tartrate, may be precipitated similarly to the potassium salts; but a more delicate test for ammonium compounds is the formation of ammonium hydroxide upon the addition of a strong base and the subsequent volatilization of ammonia gas: $NH_4^+ + OH^- = NH_4OH$ and $NH_4OH = NH_3 + H_2O$. The ammonia is detected by its odor, or by its action upon moistened red litmus paper placed over the solution. Quantitatively, ammonium salts are determined by treating the sample with excess sodium hydroxide, and distilling the ammonia into a known volume of standard acid. The excess acid is then titrated with standard base, using methyl orange as an indicator. Small amounts of ammonia are determined by means of Nessler's reagent (cf. **VIII—25**).

19. Hydrazine.—Ammonium salts may be oxidized electrolytically to hydrazine, if certain viscous substances, such as glue or starch are added to the electrolyte. Hydrazine is usually prepared by treating dilute ammonia (in the presence of glue, etc.) with chlorine to form the monochloramine, NH_2Cl; and then adding an excess of ammonia: $2NH_3 + Cl_2 = NH_2Cl + NH_4Cl$, and $2NH_3 + NH_2Cl = N_2H_4 + NH_4Cl$. The sulfate, $N_2H_4 \cdot H_2SO_4$, or $(N_2H_5)_2SO_4$, is not very soluble, and hydrazine is readily purified by crystallization as such. It may also be prepared by the reduction of the potassium sulfite-nitric oxide complex, $K_2SO_3 \cdot 2NO$, with sodium amalgam, and by the reduction of a number of organic nitrogen compounds. With water hydrazine forms the weak base, N_2H_5OH, which gives in acid solution the ion, $N_2H_5^+$. The pure substance may be prepared as a fuming liquid by distilling hydrazine hydrate with barium oxide: $N_2H_4H_2O + BaO = N_2H_4 + Ba(OH)_2$. The liquid boils at 113.5° without decomposition. Hydrazine is a

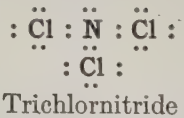
good reducing agent even in acid solution .It is oxidized quantitatively to nitrogen by iodate, chlorine, bromine, and iodine. The alkaline solution is readily oxidized by oxygen. Many oxidizing agents which gain one electron per molecule react with hydrazine to form both nitrogen and ammonia: $N_2H_5^+ + Fe^{+++} = Fe^{++} + \frac{1}{2}N_2 + NH_4^+ + H^+$. Hydrazine reacts with nitrous acid to form hydrazoic acid (Par. 21). Hydrazine is not easily reduced to ammonia. The relation of hydrazine to ammonia is analogous to that of hydrogen peroxide to water.

20. Hydroxylamine.—Hydroxylamine, NH_2OH, is best prepared by the reduction of 1 mole of nitrous acid with 2 moles of sulfurous acid (Par. **30**). The reduction is carried out at 0° in neutral solution ($NaHSO_3$) and forms first the ion of hydroxylaminedisulfonic acid: $NO_2^- + SO_2 + HSO_3^- = NOH(SO_3)_2^{--}$. This is then hydrolyzed by heating in acid solution: $NOH(SO_3)_2^{--} + 2H_2O = H_3NOH^+ + H^+ + 2SO_4^{--}$. Hydroxylamine is also obtained by the reduction of nitric and nitrous acid in dilute solution, by strong reducing agents such as tin, and zinc. The electrolytic reduction of nitric acid with most metal electrodes yields ammonia, but with a mercury cathode, hydroxylamine is formed. Hydroxylamine in solutions of acids forms the ion, NH_3OH^+, and upon evaporation of the solution, salts such as $NH_3OH \cdot Cl$, are obtained. The anhydrous compound may be prepared by distilling, under reduced pressure, an alcoholic solution of the hydrochloride with sodium methylate: $NH_3OH \cdot Cl + CH_3ONa = NH_2OH + CH_3OH + NaCl$. The melting point is 33°, and at 57°, the vapor pressure is 22 mm. At higher temperatures the liquid is very explosive. Ferric ion (in excess) in acid solution oxidizes hydroxylamine quantitatively to nitrous oxide, and more powerful oxidizing agents give nitrate. If the H^+ is low and NH_2OH is in excess, nitrogen is largely formed. Hydroxylamine is reduced by moderately powerful reducing agents, such as ferrous hydroxide, or zinc in acid solution. Aqueous solutions, especially if alkaline, decompose forming ammonia and nitrogen, or nitrous oxide.

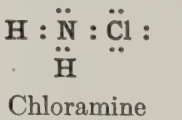
21. Hydrazoic Acid.—Nitrous oxide reacts with sodamide at about 200° to form sodium azide: $N_2\overset{\cdots}{\underset{\cdots}{O}} + H_2 : NNa = NaN_3 + H_2O$. Hydrazine and its derivatives react in the cold with nitrous acid or trichlornitride to form hydrazoic acid:

$N_2 \begin{matrix} H_4 \\ O_2 \end{matrix} NH = HN_3 + 2H_2O$. Hydrazoic acid is a somewhat stronger acid than acetic acid, and the ion, N_3^-, resembles chloride ion in the solubility of its salts and in its reversible reaction with hypochlorous acid: $HClO + HN_3 \rightleftharpoons ClN_3 + H_2O$. The product, chlorazide, like chlorine, is a gas, but is highly explosive. The iodo-azide also exists. Sodium azide tastes like sodium chloride. The free acid boils at 37°, but the warm liquid is violently explosive, as the compound is highly endothermic (62 kg. cal.). The acid reacts quantitatively with ceric ion: $2Ce^{++++} + 2HN_3 = 3N_2 + 2Ce^{+++} + 2H^+$. The crystal structure of the azides from X-ray data show that the three nitrogen atoms are in line, with a distance between the atomic centers of 1.16×10^{-8} cm. Lead azide is now used extensively in the manufacture of percussion caps.

22. Halogen Nitrides.—Trichlornitride, also called nitrogen trichloride, Cl_3N, is formed almost quantitatively by the action of excess chlorine or hypochlorous acid with ammonium ion in excess of strong acid: $NH_4^+ + 3Cl_2 = Cl_3N + 4H^+ + 3Cl^-$, and $NH_4^+ + 3HClO = Cl_3N + H^+ + 3H_2O$. With low concentration of hydrogen ion, nitrogen is evolved, probably through the reaction: $NCl_3 + NH_4^+ = N_2 + 4H^+ + 3Cl^-$. With dilute equimolal solutions of ammonia and hypochlorite, **chloramine** is formed: $NH_3 + ClO^- = NH_2Cl + OH^-$. Both substances are highly explosive, oily liquids, and are completely hydrolyzed by water to ammonia and hypochlorous acid. Because of this type of hydrolysis and the method of preparation, the nitrogen is often considered as possessing a polar valence of -3, but non-polar electronic formulae in which the electrons are shared appear more probable.



Trichlornitride



Chloramine

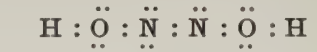
Iodine reacts with ammonia, forming a dark brown solid, the so-called **nitrogen tri-iodide,** $I_3N \cdot NH_3$. When dry, it explodes with the slightest touch. It may also be prepared by the addition of iodine chloride in concentrated hydrochloric acid to an excess of concentrated ammonia. The formation of ammonium hypoiodite, NH_4IO, appears to be an intermediate step. Bromine and fluorine react with ammonia to liberate nitrogen.

23. Nitrogen and Sulfur.—Nitrogen tetrasulfide, N_4S_4, may be prepared by the action of liquid ammonia upon sulfur, or by the action of ammonia on sulfur chloride in benzene. The compound is orange-red and may be sublimed under reduced pressure at 100°, but explodes at higher temperatures. It hydrolyzes in water to form ammonia, sulfurous, and thiosulfuric acids.

Oxides and Acids of Nitrogen

24. Nitrogen forms oxides, in which it possesses the polar valences + 1 to + 5, inclusive, and acids with the polar valences of + 1, + 3, and 5 +. In addition, there is a nitrogen peroxide, and a peroxyacid, but these are relatively unimportant. Electronic formulae are given below. These must not be interpreted as representing the actual position of the electrons, but simply as a representation of the total number of electrons and a distribution which appears to be in harmony with the known facts relating to the various compounds. The relative positions of the atoms in the molecule are known, in a majority of cases, from X-ray data on the solid crystals.

Nitrous oxide (+ 1)

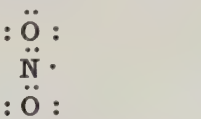


Hyponitrous acid (+ 1)

Nitric oxide (+ 2)

Nitrous anhydride (+ 3)

Nitrous acid (+ 3)



Nitrogen dioxide (+ 4)

Nitrogen tetroxide (+ 4)

Nitric anhydride (+ 5)

Nitric acid (+ 5)

25. Nitrous Oxide.—Nitrous oxide is prepared commercially by the decomposition of ammonium nitrate through gentle heating: $NH_4NO_3 = N_2O + 2H_2O$. The reaction must be carefully controlled, as overheating may result in the explosive decomposition into nitrogen, oxygen, and water. The oxide is also a product of various other reactions, including: $NH_3OH \cdot NO_2 = N_2O + 2H_2O$; $HN_3 + HNO_2 = N_2 + N_2O + H_2O$; $N_2H_4 \cdot HNO_2 = N_2O + NH_3 + H_2O$. The oxide is a colorless gas which may be liquefied by a pressure of 50 atmospheres at 20°. The critical temperature is 35°. It is soluble to the extent of 1.3 per vol. of water at 20°, and at low temperatures forms a hydrate, $N_2O \cdot 6H_2O$. Crystal structure data of the solid show all three atoms of the molecule to be in a line, with the oxygen between the nitrogen atoms.

The heat of formation of nitrous oxide is negative, about 20 kg. cal. per mole; and the gas is unstable in respect to the decomposition into its elements. However, the rate of decomposition is not appreciable at ordinary temperatures. A glowing splinter bursts into flame in nitrous oxide, and phosphorus and sulfur burn readily, nitrogen being liberated in the reaction. Strong oxidizing agents, such as permanganate, oxidize nitrous oxide to nitric oxide. Metals do not tarnish readily in nitrous oxide, and it does not combine with nitric oxide as does oxygen. The gas is employed extensively as an anaesthetic. Inhaled in small amounts, it often produces a type of hysteria, hence its common name "laughing gas." The pure liquid oxide is put on the market in heavy steel containers.

26. Hyponitrous Acid.—Hydroxylamine is oxidized by mercuric oxide or nitrous acid to hyponitrous acid: $2NH_2OH + 2HgO = H_2N_2O_2 + 2Hg + 2H_2O$; $NH_2OH + HNO_2 = H_2N_2O_2 + H_2O$. The compound is also formed by the reduction of nitric oxide or nitrous acid by strong reducing agents. The silver salt, $Ag_2N_2O_2$, is slightly soluble, and the free acid may be formed by treating the silver salt with an ether solution of hydrogen chloride. Upon evaporation of the ether, the acid is obtained as a highly explosive solid. In water solution the acid slowly decomposes into nitrous oxide and water: $H_2N_2O_2 = H_2O + N_2O$. The reaction is not reversible. The double formula is assigned from measurements of the molecular weight in various solvents.

The compound, **nitroxyl**, NOH, appears to be formed as an intermediate step in the oxidation of hydroxylamine by ferric ion in low acid, but reacts according to the equation: $NH_2OH + NOH = N_2 + 2H_2O$.

27. Nitric Oxide.—Pure nitric oxide is formed by the addition of dilute nitric acid (sp. gr. 1.2) to a boiling solution of ferrous sulfate and dilute sulfuric acid: $3Fe^{++} + 4H^+ + NO_3^- = 3Fe^{+++} + NO + 2H_2O$. It may also be formed by the reduction of dilute nitric acid by various metals, such as copper or silver, although usually contaminated by some nitrogen, nitrous oxide, or nitrogen dioxide.

Nitric oxide is highly endothermic, and is the most stable of the nitrogen oxides at high temperatures. It is formed to a small per cent in a mixture of nitrogen and oxygen in an electric arc, the reaction being the basis for the various arc processes for the fixation of nitrogen (see Nitric Acid). The oxide is also an intermediate step in another important process for the manufacture of nitric acid, namely, the oxidation of ammonia (Par. **32**).

Nitric oxide resembles nitrogen and oxygen in physical properties. The critical temperature is − 93°, and the boiling point − 150.2°. The heat of dissociation into N_2 and O_2 is − 21 kg. cal., and into atomic nitrogen and oxygen about − 190 kg. cal. It is doubtless this latter large heat that renders the rate of decomposition so slow at low temperatures. The molecule contains an odd number of valence electrons, but does now show the general tendency of such compounds to form double molecules, nor is it colored. The oxide is magnetic, its magnetic susceptibility being approximately half that of oxygen, which contains two unpaired electrons (cf. **III—3**).

At ordinary temperatures, nitric oxide reacts with oxygen or air to form brown nitrogen dioxide; but the equilibrium is reversed at higher temperatures (Table VII): $2NO + O_2 \rightleftharpoons 2NO_2$. Vigorously burning wood or phosphorus continues to burn in nitric oxide, but it does not support the combustion of more feebly burning substances, such as sulfur or a tallow candle. The oxide is somewhat soluble in water, 4.7 vol. per 100 vol. of water at 20° and 1 atm. It is, however, very soluble in solutions of ferrous salts due to the formation of the dark brown colored complex ion, $FeNO^{++}$ (cf. Par. 39). Complex ions

with cupric, cobaltous, and platinous also exist, as well as the complex sulfite, $K_2SO_3 \cdot 2NO$.

28. Nitrogen Sesquioxide, and Di- or Tetra-oxide.—The sesquioxide, N_2O_3, is the anhydride of nitrous acid: $N_2O_3 + H_2O = 2HNO_2$. The acid is very unstable and readily evolves the oxide, or, more correctly, a mixture of nitric oxide and nitrogen dioxide, since the sesquioxide is itself unstable at ordinary temperatures: $N_2O_3 = NO + NO_2$. The equimolal mixture of oxides may be condensed to a dark blue liquid boiling at 3.5°. If the liquid is completely dried, it may be vaporized without dissociation.

The dioxide, NO_2 (also incorrectly called peroxide), is largely polymerized in the liquid to tetroxide, N_2O_4. At the boiling point, 21.3°, the gaseous tetroxide is only about 20 per cent dissociated into the dioxide, but at 135° the dissociation is 99 per cent. Above 150°, the dioxide begins to dissociate into nitric oxide and oxygen.

TABLE VII

Dissociation of Nitrogen Dioxide

$t°$ C.	130	185	350	500	620
Per cent dissociated	0	5	20	57	100

The dioxide is an "odd molecule," and like the majority of such molecules, in addition to its tendency to polymerize, it is colored, the color in this case being a deep red-brown. The pure tetroxide, however, is colorless, and upon heating, therefore, undergoes a striking color change.

$$\underset{\text{Color-less}}{N_2O_4} \xrightleftharpoons{0\text{–}140°} \underset{\text{Deep brown}}{2NO_2} \xrightleftharpoons{150°\text{–}620°} \underset{\text{Color-less}}{2NO + O_2}$$

29. These oxides are involved in three important equilibria with water, nitric, and nitrous acids: (1) In small concentrations, nitrogen dioxide reacts with water in the cold to give a blue solution of nitric and nitrous acids: $2NO_2 + H_2O = HNO_2 + H^+ + NO_3^-$, $K = 10^5$. It follows from the equilibrium constant that in a dilute solution of the two acids the concentration

of nitrogen dioxide is very small. (2) Nitrous acid is unstable in respect to the decomposition: $3HNO_2 = H^+ + NO_3^- + 2NO + H_2O$, K = 30. This equilibrium is comparatively slow in cold dilute solutions, and, from the value of the constant, is rather easily reversed. (3) In warm concentrated solutions of nitric acid, the quantity of nitrous acid, which may be present, is very small, and the principal equilibrium is the following: $3NO_2 + H_2O = 2NO_3^- + 2H^+ + NO$, $K = 2 \times 10^8$. Although the equilibrium constant favors largely the formation of nitric acid from the dioxide, concentrated nitric acid may, however, be reduced by nitric oxide. The third reaction is extremely important in connection with synthetic nitric acid processes (Par. **32**). With alkaline solutions only reaction (1) occurs, i.e. nitrate and nitrite are formed and the equimolal mixture of NO and NO_2 gives almost pure nitrite.

It follows from these equilibria that the concentration of nitric acid affects greatly the reduction products of the acid. This concentration effect is illustrated by the following summary of the products formed by the action of nitric acid upon arsenous oxide:

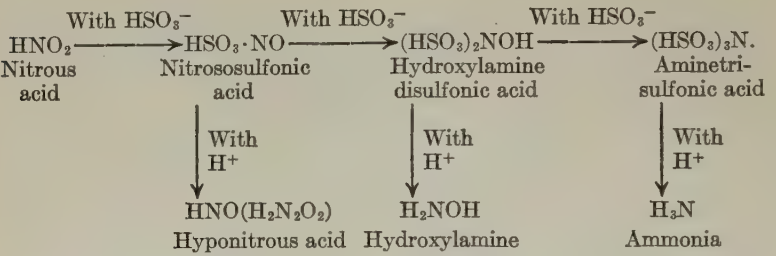
Density of HNO_3	1.20	1.25	1.35	1.45
Product.....	Almost pure NO	Mostly NO, a little NO_2	Equimolal mixture NO, NO_2	1 part NO, 10 parts, NO_2

30. Nitrous Acid and Nitrites.—The formation of nitrous acid, HNO_2, from the dioxide or sesquioxide has been discussed above. A solution containing nitrous acid may also be formed by the hydrolysis in dilute acid of nitrosylsulfuric acid: $NO_2HSO_3 + H_2O = 2H^+ + SO_4^{--} + HNO_2$. A solution of nitrous acid is conveniently formed by the addition of sulfuric acid to a nitrite in the cold. Nitrous acid is weak, the dissociation constant being 4.5×10^{-4}. The solution has a slight bluish color. The decomposition of the water solution has been discussed (Par. **29**). Nitrous acid is a rapid and fairly strong oxidizing agent:

$$NO + H_2O = H^+ + HNO_2 + E^-, \quad -0.98 \text{ volt}$$

It thus oxidizes iodide quantitatively to iodine. Strong reducing

agents are, of course, able to reduce nitrous acid to the lower valences. In general, such reductions involve a number of steps, but only in the case of sulfurous acid has the mechanism been worked out.



The reactions indicated on the horizontal are reversed in strong alkali. The reduction products may be hydrolyzed in acid solution to form the compounds indicated by the vertical arrows. The reduction potential of nitrous acid to ammonium ion is:

$$2H_2O + NH_4^+ = HNO_2 + 7H^+ + 6E^-, \quad -0.86 \text{ volts}$$

and in alkaline solution:

$$7OH^- + NH_3 = NO_2^- + 5H_2O + 6E^-, \quad +0.15 \text{ volts.}$$

Nitrous acid may also act as a reducing agent:

$$HNO_2 + H_2O = 3H^+ + NO_3^- + 2E^-, \quad -0.95 \text{ volts.}$$

A strong oxidizing agent is thus required, but the reaction is quantitative with permanganate.

Nitrites are usually prepared by heating the alkali nitrates either alone, $2KNO_3 = 2KNO_2 + O_2$, or with carbon or lead, to decrease the temperature of conversion: $2KNO_3 + C = 2KNO_2 + CO_2$.

Nitrite forms complex ions with many positive ions, including cobaltic, ferrous, chromic, cupric, platinous; the most important being that with cobaltic ion, $Co(NO_2)_6^{---}$. The alkali nitrites are extremely soluble, but the silver nitrite is but slightly soluble. The silver salt in contact with solution decomposes upon heating, according to the equation: $2AgNO_2 = Ag + NO + Ag^+ + NO_3^-$.

Nitrous acid reacts with ammonia and with organic primary amines to form nitrogen: $NH_3 + HNO_2(NH_4^+ + NO_2^-) = N_2 + 2H_2O$; $RNH_2 + HNO_2 = N_2 + ROH + H_2O$; $CO(NH_2)_2$

$+ 2HNO_2 = 2N_2 + CO_2 + 3H_2O$. The reaction with urea, $CO(NH_2)_2$, is often employed to remove nitrites from solution. Nitrous acid forms nitrosoamines with secondary amines: $R_2NH + HNO_2 = R_2N \cdot NO + H_2O$. With aniline hydrochloride in the cold, nitrous acid forms diazonium chloride: $C_6H_5NH_2 \cdot HCl + HNO_2 = C_6H_5N_2Cl + 2H_2O$. This reaction is important in the synthesis of many organic compounds. Due to the weakness of nitrous acid, soluble nitrites are slightly hydrolyzed. Nitrites are readily distinguished from nitrates by the fact that ferrous ion is oxidized in dilute acid (acetic) by nitrite, but not by nitrate, to give the characteristic brown color of the $Fe(NO)^{++}$ ion.

31. Nitric Acid.—Pure nitric acid is a colorless liquid, density 1.54, freezing point − 47°, boiling point 86° under atmospheric pressure, and 35° under pressure of 20 mm. The concentrated acid is usually colored yellow, due to the presence of a percentage of the dioxide formed by the slow decomposition: $4HNO_3 = 4NO_2 + 2H_2O + O_2$. The speed of the decomposition is increased by higher temperature and by light. The acid fumes strongly in moist air; the water solution has a constant boiling mixture of 68 per cent acid, density 1.41, and boiling point of 120.5°. Upon repeated distillation of the pure acid, the constant boiling mixture is obtained through the formation of water by the decomposition reaction.

The **anhydride or pentoxide** may be formed by the action of phosphorus pentoxide upon concentrated nitric acid: $2HNO_3 + P_2O_5 = N_2O_5 + 2HPO_3$. It is a white solid which readily sublimes, and is easily decomposed into the dioxide and oxygen. The freezing point composition curves for the acid and water show the existence of mono-, di- and tri-hydrates at low temperatures. Water solutions of nitric acid are highly ionized (Append. IV).

32. Three processes for the **manufacture of nitric acid** are now in use: (1) the older process of preparation from Chile saltpeter and sulfuric acid, (2) from nitric oxide formed by the oxidation of ammonia, (3) from nitric oxide formed by the direct union of the elements.

For many years, Chile saltpeter (cf. **IV—23**) was practically the only source of nitric acid. The acid is produced from the salt by heating with concentrated sulfuric acid: $NaNO_3 + H_2SO_4$

$= HNO_3 + NaHSO_4$. The reaction proceeds because of the greater volatility of nitric acid, and is carried out under reduced pressure in order to operate at the lowest possible temperature, and thus keep down the decomposition of the acid. The reaction mixture is heated in iron retorts, and nitric acid condensed and collected in glass tubes and vessels. The sodium acid sulfate is valuable because of its acid properties, and is used in various industries.

Since it is now possible to make ammonia synthetically at as low a cost per pound of nitrogen as Chile nitrate can be mined and extracted, ammonia appears destined to become the principal commercial source of the acid. The oxidation is carried out by passing a mixture of ammonia (about 10 per cent) and air over a heated platinum gauze: $4NH_3 + 5O_2 = 4NO + 6H_2O$. The platinum gauze is maintained at a temperature of 900–1000° C. The gaseous mixture is heated to about 300° before entering the catalyst, and the heat of oxidation is sufficient to maintain the catalyst at the high temperature once the reaction is started. The efficiency of oxidation is about 96 per cent of the ammonia. The gas from the catalyst passes into absorption towers: $2NO + O_2 = 2NO_2$ and $3NO_2 + H_2O = 2HNO_3 + NO$. The first of these reactions is rather slow, but is catalyzed by most surfaces. The second reaction has been discussed at length under the oxide. The final two or three per cent of the oxide is absorbed in sodium carbonate solution to give a mixture of nitrate and nitrite. An important factor in the successful development of the process has been the use of chrome-steel alloys in the absorption towers, as this metal is practically unattacked by nitric acid.

33. The synthesis of nitric acid from its elements can only be carried out at extremely high temperatures as indicated in Table VIII.

TABLE VIII

EQUILIBRIUM IN THE REACTION $N_2 + O_2 = 2NO$

$t°$ C.	1227	1727	2227	2627	2927	3927
Per cent of $N_2 + O_2$ combined	0.1	0.6	1.8	3.2	4.2	10.0

The existence of nitric oxide at ordinary temperatures is

obviously due to a very slow rate of decomposition, and this rate becomes rapid only at high temperatures.

TABLE IX

Estimated Time Required for Half Decomposition of NO

$t°$ C.	721	1227	1627	1827	2627
Time	81.6 years	1.3 days	2.1 min.	5.1 sec.	3×10^{-5} sec.

A process for the direct synthesis of nitric oxide must, then, involve the heating of a mixture of oxygen and nitrogen to about 2000° C., followed by the rapid cooling of the equilibrium mixture. This is carried out commercially (chiefly in Norway) by blowing the gases through an electric arc. In the Badesche process, an arc through a 20-foot tube is employed. The gases pass through the arc and are cooled rapidly by coming in contact with the walls of the tube. The Birkeland-Eyde process employs alternating discharges between electrodes placed at right angles to the poles of an electro magnet which results in a broad disk-shaped arc. The nitric oxide is absorbed as discussed above in the ammonia process. Under the best working conditions, the yield of nitric oxide is only about 2.5 per cent, and it is doubtful if the process can continue to compete with nitric acid from ammonia, even in countries where electrical power is very cheap. The yield is somewhat greater than is to be expected from the equilibrium values, doubtless due to the direct absorption of electrical energy by nitrogen to form activated molecules. Most of the nitric acid produced by the Norwegian plants is converted into calcium nitrate by absorption in lime and sold as fertilizer.

34. Nitric Acid as an Oxidizing Agent.—The conditions for the reduction of nitric acid to NO, NO_2^-, or NO_2 have been discussed (Par. **29**). The values for a number of the oxidation-reduction potentials at molal concentration are given below, but it must be pointed out that in the majority of the reactions the rates are slow, and that the speed becomes a factor of equal importance with the energy in determining what reactions will occur.

TABLE X

OXIDATION-REDUCTION POTENTIALS OF HNO_3 AND NO_3^-

	Volts$_{25°}$
$H_2O + NO_2 = NO_3^- + 2H^+ + E^-$	− 0.79
$H_2O + HNO_2 = NO_3^- + 3H^+ + E^-$	− 0.95
$2OH^- + NO_2 = NO_3^- + H_2O + 2E^-$	− 0.0
$2H_2O + NO = NO_3^- + 4H^+ + 3E^-$	− 0.94
$3H_2O + \frac{1}{2}N_2 = NO_3^- + 6H^+ + 5E^-$	− 1.24
$3H_2O + NH_4^+ = NO_3^- + 10H^+ + 8E^-$	− 0.77
$9OH^- + NH_3 = NO_3^- + 6H_2O + 8E^-$	+ 0.12

Although the reduction to free nitrogen appears to give the greatest potential, this reaction is seldom realized, and then only through the formation, first, of a compound of nitrogen of negative polar valence number which reacts with nitrogen compounds of the same positive valence number, e.g. $NH_4^+ + NO_2^- = N_2 + H_2O$ and $NH_2OH + NOH = N_2 + 2H_2O$ (Par. **26**). The values in the table show that nitrate in alkaline solution is not a powerful oxidizing agent. The values in the table apply to molal concentrations and cannot be used to predict the action of concentrated nitric acid, which is a far more powerful oxidizing agent, especially when heated. Nitric acid is reduced by sulfurous acid or acid sulfites through the formation of nitrosylsulfuric acid, $HONO_2 + H_2SO_3 = HSO_3 \cdot NO_2 + H_2O$, and its subsequent hydrolysis in dilute acid: $HSO_3 \cdot NO_2 + H_2O = HNO_2 + H_2SO_4$. (See Par. **31** for continuation of reduction process.)

35. Nitric acid reacts with chloride ion according to the equation: $4H^+ + NO_3^- + 3Cl^- = NOCl + Cl_2 + 2H_2O$. The compound, NOCl, is **nitrosyl chloride**, a liquid boiling at − 5.6°, and unstable with respect to its decomposition into nitric oxide and chlorine. The mixture of nitric and hydrochloric acids, known as **aqua regia**, is capable of dissolving gold and platinum, which will not dissolve in nitric acid alone. This, however, is not due to an increase in the oxidizing potential of the nitric acid in the presence of the chloride, but rather to an increase in the reduction potential of these metals in the presence of the chloride (cf. **VII—31**).

36. Nitric acid reacts with organic hydroxides to form nitrates, for example with glycerine to form "nitroglycerine," $C_3H_5(OH)_3 + 3HNO_3 = C_3H_5(NO_3)_3 + 3H_2O$, and with hydrocarbons, such as benzene, to form nitro compounds such as nitrobenzene:

$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O$. In both of these reactions, water is produced, so that the reaction is favored by the presence of concentrated sulfuric acid to lower the activity of this product. Large quantities of the mixed concentrated acids are manufactured for this purpose. At present, the major portion of the nitric acid manufactured is consumed in some form of organic nitrate or nitro-compound, the more important being the explosives, plastics, varnishes, and dyes (cf. **XIII—29**).

37. Nitrates.—The nitrates of the metals are, in general, readily soluble in water. The nitrate group shows but slight tendencies to form coordination compounds. The alkali nitrates decompose upon heating to form nitrites: $2NaNO_3 = 2NaNO_2 + O_2$. The nitrates of the more noble metals form the dioxide, e.g. $2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$. Ammonium nitrate decomposes into nitrous oxide and water: $NH_4NO_3 = N_2O + 2H_2O$.

X-ray data on the crystalline nitrates show that the three oxygen atoms are arranged symmetrically about the nitrogen atom but the centers of the atoms do not appear to be in the same plane.

The properties of many nitrates have been discussed under the various positive constituents, the more important being the salts of sodium, potassium, ammonia, and calcium. Formerly the largest use of a nitrate was in the manufacture of **gunpowder,** consisting of potassium nitrate, 75 per cent; charcoal, 15 per cent; and sulfur 10 per cent. This mixture is moistened, ground, and the dried product granulated. When ignited, the powder burns and liberates a large volume of gases consisting mainly of nitrogen, carbon dioxide, carbon monoxide, and some sulfur dioxide. This type of powder is not smokeless, since solid particles of potassium sulfide and oxide are dispersed in the gas phase.

38. Peroxynitrogen Compounds.—Nitric oxide appears to unite with oxygen at low temperature ($-180°$) to form the peroxide, NO_3, which decomposes upon heating. The silver salt of the peroxynitric acid, HNO_5, is said to be formed by the electrolysis of a concentrated solution of silver nitrate, but neither the free acid nor other salts have been prepared. The highly unstable acid, HNO_4, is formed by the action of hydrogen peroxide upon nitrogen pentoxide: $H_2O_2 + N_2O_5 = HNO_4 + HNO_3$.

39. Analytical.—The ferrous sulfate test for nitrates depends upon the reduction of nitrates by ferrous ion in concentrated hydrogen ion solution and the formation of the brown complex ion, $Fe(NO)^{++}$. The test may be carried out by the addition of an equal volume of concentrated sulfuric acid to a few cc. of unknown solution. When this solution has cooled, a solution of ferrous sulfate is added with the tube inclined so that the liquids do not mix. A brown ring at the junction of the two liquids indicates nitrate. The test is not satisfactory in the presence of chlorate, iodine, bromine, nitrite, ferrocyanide, or ferricyanide. The diphenylamine test for nitrates consists of the addition of a solution of $(C_6H_5)_2NH$ in sulfuric acid to 2 or 3 cc. of unknown solution on a watch glass. Upon gentle heating, a blue color is produced if a nitrate is present.

The quantitative determination of nitrate is usually carried out either by reduction to ammonia and the determination as such, or the reduction to nitric oxide, and its estimation as a gas (nitrometer method). In the former process, aluminum or Devarda's alloy (Al 45, Cu 50, Zn 5) in alkaline solution is used as the reducing agent. The ammonia is distilled into excess standardized sulfuric acid, and the excess of acid titrated with sodium hydroxide. The nitrometer process depends upon the reaction: $2NO_3^- + 8H^+ + 3SO_4^{--} + 6Hg = 3Hg_2SO_4 + 4H_2O + 2NO$. The nitric oxide is collected in a gas burette or nitrometer and the quantity of nitrate calculated from the volume of gas. The base diphenylendoanilohydrotriazole, $C_{20}H_{16}N_4$, called **nitron,** forms a slightly soluble nitrate, $C_{20}H_{16}N_4 \cdot HNO_3$, and this reagent can be used for the quantitative separation and estimation of nitric acid.

PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH

40. The elements of this group form an especially interesting series in that they involve a complete transition from non-metallic to metallic character in both physical and chemical properties. It is, however, noteworthy that this transition is by no means uniform, but that there is rather an alternation in properties. Thus, nitrogen, arsenic and bismuth form no pentachlorides, while phosphorus and antimony do. Figure 1 illustrates this alternation for the heats of formation of the trioxides and trichlorides when plotted against atomic numbers. This alter-

nation extends to neighboring groups, as illustrated first by figures for the heats of formation of the dioxides of Group VI and second, in Group VII, by the existence of oxides of chlorine and iodine, but not of fluorine or bromine. Various other evidences of alternation may be discovered, such as the enhanced tendency towards hydration of the oxides of phosphorus and antimony as compared with those of their immediate neighbors.

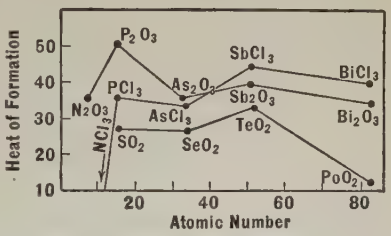


FIG. 1.—Heats of formation in kg. cal. per equivalent against atomic numbers.

41. Occurrence.—Phosphorus is the only member of the group which is never found free in nature. It occurs principally as calcium phosphate, $Ca_3(PO_4)_2$, and as apatite, $Ca_5F(PO_4)_3$ and $Ca_5Cl(PO_4)_3$. The first of these is found in large deposits of phosphate rock in Florida, Tennessee, Montana, and neighboring states, and in northern Africa. It is the principal mineral constituent of bones and teeth, and bone ash is largely calcium phosphate. Apatite occurs in many rocks, and important deposits are located in Canada. Many plant and animal tissues contain phosphoproteins, complex compounds of protein with phosphoric acid derivatives, such as casein in milk, and vitellin in eggs. The average human body daily excretes phosphorus compounds containing about 2 g. of the element.

Arsenic and antimony are occasionally found free, and bismuth is generally so found. Their most important minerals are the sulfides: arsenical pyrite, FeAsS; orpiment, As_2S_3; realgar, As_2S_2; stibnite, Sb_2S_3; bismuthinite, Bi_2S_3. Oxides also occur such as claudetite, As_2O_3; senarmontite, Sb_2O_3; and bismite, $Bi_2O_3 \cdot H_2O$, and less frequently selenides and tellurides. Arsenides, such as $FeAs_2$, $CoAs_2$, and NiAs are not infrequent, and arsenic is a common impurity in sulfuric acid made from pyrites, in pig iron, and in commercial zinc. The most extensive deposits of antimony are located in China.

42. Properties of the Elements.—The more important physical constants are summarized in Table XI. Like the corresponding elements of Group VI, phosphorus, arsenic and antimony exist in a number of crystalline modifications. **Phosphorus** has the

two familiar forms known as "**white**" and "**red.**" The white modification is formed by rapidly cooling phosphorus vapor. It is a wax-like substance, of low melting point, very low heat of fusion (157 cal. per g. atom), high volatility even at room temperature (Fig. 2) and is readily soluble in carbon disulfide (90 g. per 100 g. sol. at 10°). It ignites spontaneously in air and is, therefore, usually kept and worked under water in which it is only very slightly soluble (1 in 300,000). It is extremely poisonous, about 0.1 g. being a fatal dose, and the continued consumption of small amounts leads to chronic poisoning, one of the symptoms of which is necrosis of the jaw. The white is a metastable form and upon heating or exposure to sunlight turns yellow and then red. The transition is catalyzed by iodine: a trace of the latter causes a very rapid reaction at 200°. The heat of the transition is 3,700 cal.

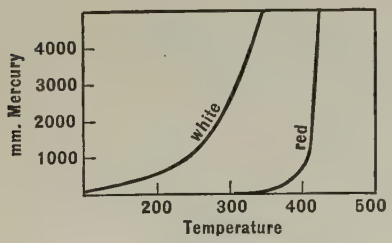


FIG. 2.—Vapor pressure of phosphorus.

The red modification does not have definite density or melting point and appears to be a transition form or mixture of the white and the real stable modification, **violet phosphorus.** The latter is difficult to prepare pure, but may be obtained by crystallization from a solution in molten lead. The properties of red phosphorus are essentially those of the violet. It is much less volatile than the white and is not appreciably soluble in carbon disulfide or other solvents. Red phosphorus sublimes without melting, unless heated under pressure, and from the shape of the vapor pressure curves there does not appear to be a transition point between the two modifications. Red phosphorus is not especially reactive, only slightly poisonous, and does not ignite below 240°. White phosphorus has a molecular weight corresponding to P_4 in its solutions and in the vapor state, but the red or violet is not sufficiently soluble to enable its molecular weight to be determined. Above 1500°, the vapor is somewhat dissociated into P_2. A third solid modification, **black phosphorus,** is formed when a pressure of 4,000 atmospheres is applied to the element at 200°.

Arsenic exists in a reactive metastable crystalline modification,

the so-called "yellow" arsenic, and a grey semi-metallic form. **Yellow arsenic** is formed by passing the vapor into cold carbon disulfide. The rate of transition into the grey form is rapid even at low temperature and instantaneous at room temperature in the sunlight. Yellow arsenic volatilizes readily, is extremely poisonous and phosphoresces in air at room temperature. Its molecular weight in solution corresponds to As_4. The **metallic form** is steel grey in color with a bright lustre, very brittle, and is a good conductor of heat but a rather poor electrical conductor. It sublimes without melting unless heated under pressure.

Antimony occurs in modifications similar to those of arsenic. **Yellow antimony** is transformed so rapidly into the stable form that it can be kept only at low temperature. Antimony also forms a metastable metallic modification known as **explosive anitmony** from the character of its transition into the stable form when struck or scratched. The reaction evolves 20 cal. of heat per gram. Yellow antimony is formed by the action of oxygen upon liquid stibine, SbH_3, at $-90°$, and the explosive form by the electrolysis of a concentrated solution of antimony trichloride. The explosive form always contains some trichloride, and is probably a solid solution of the chloride in yellow antimony. The stable modification is a silvery white, metallic appearing substance. It is extremely brittle and much less volatile than arsenic.

Bismuth is known only in the one crystalline metallic form. It is grey white with a slight red tinge, hard and brittle, a very poor conductor of heat, and, although its melting point is low, the boiling point is high.

43. Preparation of the Elements.—Phosphorus is generally prepared from calcium phosphate through the reaction, $Ca_3(PO_4)_2 + 3SiO_2 + 5C = 3CaSiO_3 + 5CO + P_2$, which is carried out at high temperatures, usually in an electric arc furnace. Phosphorus vapor leaves the furnace along with the carbon monoxide and is condensed under water, while the calcium silicate is drawn off as liquid slag. The element was first prepared by Brandt in 1669, by the destructive distillation of the solid residue from the evaporation of urine.

Arsenic, antimony, and bismuth may be obtained by the reduction of the oxides with carbon, e.g. $As_2O_3 + 3C = 2As + 3CO$. In case the ore is a sulfide, it may first be roasted to

the oxide: $2As_2S_3 + 9O_2 = 2As_2O_3 + 6SO_2$; or iron may be used as the reducing agent: $Sb_2S_3 + 3Fe = 2Sb + 3FeS$. Native bismuth is easily extracted by taking advantage of its low melting point, and simply heating the ore and running off the metal.

TABLE XI

ATOMIC AND PHYSICAL PROPERTIES OF PHOSPHORUS, ARSENIC, ANTIMONY AND BISMUTH

	P	As	Sb	Bi
Atomic weight	31.027	74.96	121.77	209.00
Atomic number	15	33	51	83
Isotopes	None	None	121, 123	209, 210, 214
Electrons in various quantum states, 1st	2	2	2	2
2d	8	8	8	8
3d	5	18	18	18
4th		5	18	32
5th			5	18
6th				5
Ionization of gaseous atom, volts	13.3	11.5	9 ?	8.0
Size of M^{+5} ion, cm. $\times 10^8$ (if $Cl^- = 1.81$)	0.34	0.47	0.62	0.74
Molecular formula of gas at boiling point	P_4	$As_4 - As_2$	$Sb_2 - Sb$	$Bi_2 - Bi$
Melting point	W 44.1° V 590(43 atm.)	814°(36 atm.)	630.5°	271°
Boiling point	280°	615°(sub.)	1380°	1450°
Density	W 1.82 V 2.34	M 5.7 Y 3.9	M 6.58 Y 5.3	9.8
Electrical resistivity, ohm-cm	W 10^{11}, 10°	35×10^{-6}, 0°	39×10^{-6}, 20°	115×10^{-6}, 20°
$G + 4H_2O = H_3GO_4 + 5H^+ + 5E^-$: Potential in volts.	ca 0.3	−0.34	−0.3	−0.8
$G + 3H_2O = H_3GO_3 + 3H^+ + 3E^-$	ca 0.3	−0.24	0.0	$Bi = Bi^{+++} + 3E^-$, −0.2

44. Commercial Applications of the Elements.—Most of the phosphorus manufactured is consumed in the preparation of the sulfide, P_4S_3 (Par. 62), for use in matches. Formerly matches were made by dipping wood splints into a paste containing white phosphorus, lead dioxide, powdered glass, and glue. Due to its poisonous nature, the use of white phosphorus is now prohibited in most countries and in its place the trisulfide is substituted. When struck, the friction raises the temperature to the point where the phosphorus sulfide is rapidly oxidized by the lead dioxide and the match bursts into flame. In the so-called "bird's eye" match, the phosphorus sulfide is present only in the small tip. The safety matches now used so extensively contain no phosphorus in the match head, but the box is coated with a mixture of red phosphorus, glue, and abrasive. The match contains a mixture of good oxidizing agents, such as

potassium chlorate or chromate, and reducing agents, as antimony sulfide. It may be ignited by striking on some surface of low heat conductivity, such as glass, and more readily on the surface of the box, since a trace of the red phosphorus is ignited by the friction and the heat kindles the match head.

Phosphorus was used in the great war in tracer bullets and burning phosphorus was employed for the preparation of smoke screens. Ground with flour and grease, white phosphorus is used as a poison for rodents.

Very little free arsenic is consumed. A small amount of element (0.5 per cent) is usually added to lead in making shot to harden it and also to increase the surface tension. The latter aids in obtaining perfect spheres when the shot is made by allowing molten drops to fall from a height. The trioxide is an important commercial compound.

Antimony is a cheap metal which can be used in certain instances as a substitute for more expensive metals. Most of the world's supply comes from China. The annual consumption in the United States is about 20,000 tons. Its principal use is in the manufacture of alloys, especially those of lead and tin, the most important being type metal, white metal, hard metal, britannia, babbitt, and antifriction metal (see Alloys of Lead and Tin). The presence of antimony adds to the hardness of the metal and also contributes the property of expanding upon solidification, which makes these alloys very useful in the preparation of sharp castings.

Bismuth alloys also expand upon cooling and make good castings. A number of bismuth alloys can be prepared which melt below the boiling point of water, e.g.

	M.P.	Bi	Pb	Sn	Cd
Lipowitz metal	60°	50	37	13	10
Woods metal	71°	50	25	12.5	12.5
Rose metal	94°	50	27.1	22.9	—

Alloys of this type are used in automatic fire extinguishers which depend upon plugs of the alloy melting and releasing water sprinklers, closing fire-doors, etc. Such alloys are also employed in safety plugs in steam boilers to guard against overheating.

45. Reactions of the Elements.—The reactions of phosphorus are markedly different for the two modifications. Yellow phosphorus in moist air at ordinary temperature emits a pale greenish light and gives off white fumes of the sesquioxide, and the reaction is accompanied by the formation of ozone. The light is not true temperature radiation but results from the conversion of some of the reaction energy directly into light (**chemiluminescence**). The glow appears to be connected with the formation of trioxide and does not occur if the partial pressure of the oxygen is considerably increased, although oxidation to the pentoxide then takes place. Yellow phosphorus ignites at about 45°, the red at about 260°. The yellow modification likewise ignites spontaneously in chlorine, but the red must be heated to start the reaction. Yellow phosphorus is also soluble in hot alkalies liberating phosphine while the red is not. Sulfur reacts with phosphorus forming sulfides and with the halogens (Par. **61**). Moderately strong oxidizing agents oxidize phosphorus to phosphoric acid; $P + 4H_2O = H_3PO_4 + 5H^+ + 5E^-$; $+ 0.3$ volt (approximately). The potential value indicates that even hydrogen ion should be capable of oxidizing the element but the oxidation appears to be slow with all weak oxidizing agents.

Arsenic, antimony, and bismuth form surface films of oxide in moist air, and burn to the trioxide when heated (Sb also forms some Sb_2O_4). Like phosphorus, they unite directly when heated with sulfur (Par. **62**), the halogens (Par. **61**), and various metals (Par. **63**). The oxidation of the elements to the pentavalent state becomes increasingly difficult with increasing atomic weight. Concentrated nitric acid, acting upon the elements, forms H_3AsO_4, Sb_2O_5, and $Bi(NO_3)_3$. The reactions are summarized in Table XII.

TABLE XII

REACTIONS OF PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH
(G = any element of the group)

$4G + 3O_2 = 2G_2O_3$	See also P_2O_5 and Sb_2O_4
$2G + 3X_2 = 2GX_3$	X = halide. See also Par. **61** for GX_5, etc.
$2G + 3S = G_2S_3$	See Par. **62** for other sulfides
$nM + mG = M_nG_m$	Formation of metal phosphides, arsenides, antimonides and bismuthides
$G + 4H_2O = H_3GO_4 + 5H^+ + 5E^-$	See Table XI

46. Hydrogen Compounds.—Gaseous hydrogen compounds the analogues of ammonia, are formed by all members of the group: **phosphine,** PH_3; **arsine,** AsH_3; **stibine,** SbH_3; **bismuthine,** BiH_3. They are frequently referred to as hydrides, but since the hydrogen is undoubtedly more positive, the name does not appear to be appropriate.

TABLE XIII

PHYSICAL PROPERTIES OF HYDROGEN COMPOUNDS

	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Melting point, °C.....	−75	−132.5	−119	−88	?
Boiling point, °C.....	−33.5	− 86.2	− 55	−18	?
Heat of formation, Kg. Cal.....	10.2	4.9	− 36.7	−81.8	?

47. Unlike ammonia, the other members of the group cannot be prepared by the direct union of the element and hydrogen, although phosphine appears to be stable at room temperature, since the heat of formation from yellow phosphorus, as given above, is positive, and the free energy of formation can hardly be sufficiently different to render the compound unstable. Phosphine decomposes readily, however, upon heating; stibine decomposes explosively and the bismuth compound is so unstable that only traces of it can be prepared. The decomposition of arsine and stibine is further considered under the Marsh test (Par. **64**).

A general method of preparation is the hydrolysis of a binary metal compound similar to the hydrolysis of magnesium nitride to form ammonia: $Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + 2PH_3$; $Na_3As + 3H_2O = 3NaOH + AsH_3$; $Zn_3Sb_2 + 6H_2O = 3Zn(OH)_2 + 2SbH_3$; $Mg_3Bi_2 + 6H_2O = 3Mg(OH)_2 + 2BiH_3$.

Phosphine may also be prepared by boiling white phosphorus with a solution of an alkali: $4P + 3OH^- + 3H_2O = 3H_2PO_2^- + PH_3$. There are usually present in the gas traces of the compounds P_2H_4 and P_4H_2.

Arsine may be formed by cathodic reduction, or by the reduction of arsenic compounds in acid solution by zinc or magnesium: $H_3AsO_3 + 3Zn + 6H^+ = AsH_3 + 3Zn^{++} + 3H_2O$. This reduction gives, of course, a mixture of the gas and hydrogen.

The same method is also applicable to the preparation of stibine.

These compounds are all extremely poisonous and it is dangerous to inhale even small amounts. Due to the presence of arsenic in many acids and metals, arsine is a common impurity in hydrogen prepared through their interaction, and such hydrogen should, therefore, not be inhaled unless it has been passed through permanganate solution.

Pure phosphine does not ignite spontaneously in air unless heated to about 100°, but as ordinarily prepared it inflames spontaneously, due to the presence of some of the liquid hydrogen phosphide, P_2H_4. The gas burns to phosphoric acid: $PH_3 + 2O_2 = H_3PO_4$. If bubbled through water into air, the bubbles ignite at the surface and form beautiful smoke rings. Arsine and stibine readily burn in air, forming the trioxides. If, however, a piece of cold porcelain is placed in the flame, it is coated with the free element. The liquid compound, P_2H_4, decomposes in the light into phosphine and a hydrogen phosphide, P_4H_2, or possibly $P_{12}H_6$, which is a solid: $5P_2H_4 = 6PH_3 + P_4H_2$.

48. Unlike ammonia, these compounds are only slightly soluble in water (PH_3, 11 vol. in 100 vol. water at 15°), and the solutions are not alkaline. The basic nature of the compounds decreases with the increasing size of the elements. Indeed, phosphine is the only one which resembles ammonia in the formation of salts, the **phosphonium compounds,** and these are far less stable than the ammonium compounds.

Phosphonium iodide, PH_4I, is formed by the reaction: $PH_3 + HI = PH_4I$. It crystallizes in beautiful, large, highly refracting, square, prisms which sublime at 62°. It is a powerful reducing agent, and is decomposed by water with the liberation of phosphine. Phosphonium bromide resembles the iodide, but the chloride can only be formed at room temperature under pressure (at 14° the dissociation pressure, $PH_4Cl = PH_3 + HCl$, is about 20 atmospheres).

Phosphine reacts with solutions of certain metallic ions, e.g. Cu^{++}, with the formation of nearly insoluble metal phosphides, which usually are of uncertain composition. Arsine passed into a solution of silver nitrate gives metallic silver and arsenious acid: $AsH_3 + 6Ag^+ + 3H_2O = 6Ag + H_3AsO_3 + 6H^+$. Under the same conditions, stibine gives silver antimonide: SbH_3

$+ 3Ag^+ = 3H^+ + Ag_3Sb$. Arsenic forms no compounds analogous to hydrazine but organic derivatives are known, such as $As_2(CH_3)_4$, **cacodyl.**

Oxides and Acids

49. The oxides and acids are summarized in Table XIV.

TABLE XIV

Acids and Oxides of Phosphorus, Arsenic, Antimony, and Bismuth

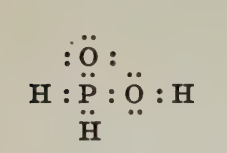
Valence		P	As	Sb	Bi
	Oxides				
2	Monoxide	.....	.....	.....	BiO
3	"Trioxide" (or X_4O_6)	P_2O_3	As_2O_3	Sb_2O_3	Bi_2O_3
4	Tetroxide	P_2O_4	As_2O_4(?)	Sb_2O_4	Bi_2O_4(?)
5	Pentoxide	P_2O_5	As_2O_5	Sb_2O_5	Bi_2O_5
	Acids				
1	Hypo-us	H_3PO_2	.....	.....	.....
3	-ous meta	.....	$HAsO_2$	$HSbO_2$	.....
	-ous ortho	H_3PO_3	H_3AsO_3	H_3SbO_3	$Bi(OH)_3$
	-ous pyro	$H_4P_2O_5$	.....	.....	.....
4	Hypo-ic	$H_4P_2O_6$	.....	.....	.....
5	-ic meta	HPO_3	$HAsO_3$	$HSbO_3$	$HBiO_3$
	-ic ortho	H_3PO_4	H_3AsO_4	H_3SbO_4	.....
	-ic pyro	$H_4P_2O_7$	$H_4As_2O_7$	$H_4Sb_2O_7$	.....

Although the tetroxides of arsenic and bismuth are described, they may be mixtures of the tri- and pentoxides. Peroxyacids of phosphorus, $H_4P_2O_8$ and H_3PO_5, also exist. The pentoxides, with the exception of that of phosphorus, readily evolve oxygen upon heating, forming the sesquioxides. These oxides are formed also upon burning the elements in air. Measurements of gas density show that the sesquioxides, generally called the trioxides, are associated into double molecules, X_4O_6. Phosphorus pentoxide has an enormous affinity for water, even removing it from concentrated sulfuric acid. The oxides of arsenic react slowly with water, while the oxides of antimony and bismuth show almost no such reaction. With increasing size of the atoms, the oxides become less acidic.

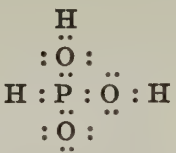
50. Oxides and Acids of Phosphorus.—The sesquioxide, P_2O_3, is produced by the combustion of phosphorus in a limited supply of air. It dissolves slowly in cold water, to form phosphorous acid, and violently in hot water, to form phosphoric acid and

phosphine: $2P_2O_3 + 6H_2O = PH_3 + 3H_3PO_4$. When heated in a sealed tube, it decomposes into the tetraoxide and phosphorus: $4P_2O_3 = 3P_2O_4 + 2P$. The trioxide is readily separated from the pentoxide by the greater volatility of the former. The heat of formation of P_2O_5 from its elements is about 370 kg. cal., and the heat of solution in water to form orthophosphoric acid, H_3PO_4, is about 35 kg. cal. The pentoxide appears to exist in a number of forms, one of which sublimes at about 350°. The vapor density of the higher oxide corresponds to the formula P_4O_{10} even at 1500°. Frequent mention has been made of the oxide as an extremely efficient drying agent.

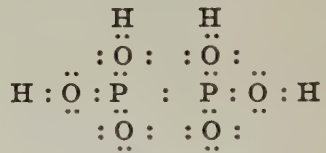
Electronic formulas for the more important phosphorus acids are given below:



Hypophosphorous acid

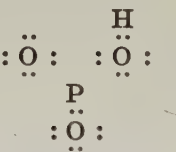


Phosphorous acid



Hypophosphoric acid

Orthophosphoric acid



Metaphosphoric acid

Pyrophosphoric acid

The formulas for hypophosphorous acid and phosphorous acid have been written with two and one hydrogen atoms, respectively, attached to the phosphorus. This is in agreement with the fact that the former acts only as a monobasic acid and the latter generally as a dibasic acid, and also that these acids are fairly strong (even stronger than phosphoric acid—see Table XV), whereas the general rule that the higher the positive valence number, the stronger the acid, would predict that they would be very weak acids, since phosphoric acid is, itself, only moderately strong. In other words, it seems probable that the hydrogen attached to phosphorus serves to attract electrons, and thus increase the effective charge on the central atom.

TABLE XV

CONDUCTIVITY OF PHOSPHORUS ACIDS

	H_3PO_2	H_3PO_3	H_3PO_4
Equivalent Conductivity.....	281	257	156

51. Salts of **hypophosphorous acid,** $H(H_2PO_2)$, are obtained by the action of phosphorus on an alkaline solution (Par. 47). The free acid may be prepared by treating the barium salt with sulfuric acid. The acid is a strong reducing agent:

$$H_3PO_2 + 2H_2O = H_3PO_4 + 4H^+ + 4E^-, + 0.48 \text{ volt.}$$

When heated, it decomposes into phosphine and phosphoric acids. The sodium salt, NaH_2PO_2, is used in medicine under the belief that phosphorus can thus be supplied to the body tissues. As mentioned above, the acid is monobasic and highly ionized in solution.

52. **Phosphorous acid,** $H_2(HPO_3)$, is formed by the action of the trioxide upon cold water, or by the hydrolysis of the trichloride: $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$. The further addition of the chloride gives the pyro-acid, $H_4P_2O_5$. The acid decomposes upon heating to give pure phosphine and phosphoric acid. The acid is oxidized to phosphoric acid by weak oxidizing agents, such as mercurous chloride:

$$H_3PO_3 + H_2O = H_3PO_4 + 2H^+ + 2E^-, + 0.3 \text{ volt.}$$

53. **Hypophosphoric acid,** $H_4P_2O_4$, may be formed, mixed with phosphorous acid, by the slow oxidation of phosphorus in a limited supply of moist air. It is tetrabasic, and its salts are relatively unimportant.

54. **The Phosphoric Acids and Phosphates.**—The product of the addition of phosphorus pentoxide to an excess of water is a solution of the orthophosphoric acid, H_3PO_4. This acid, or its hydrate, $2H_3PO_4 \cdot H_2O$, may be crystallized from the solution by evaporating under reduced pressure. The pure acid melts at 42.3° and the hydrate at 29.4°. The acid is tribasic, and thus forms three series of salts. The ionization constants for the acid are, respectively, $k_1 = 1.1 \times 10^{-2}$, $k_2 = 2.0 \times 10^{-7}$, $k_3 = 3.6 \times 10^{-13}$. The values for the molal concentration of H^+

in molal solutions of the following are: H_3PO_4, 0.1; NaH_2PO_3, 2×10^{-4}; Na_2HPO_4, 10^{-8}; Na_3PO_4, 10^{-13}.

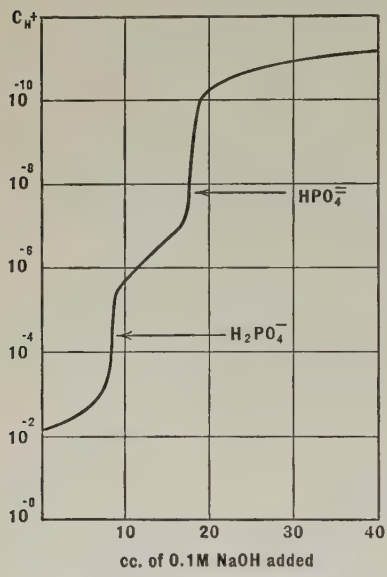


FIG. 3.—Titration curves for phosphoric acid.

Phosphoric acid is but a very weak oxidizing agent (Table XII). In this respect, it differs greatly from the other pentavalent acids of the group.

Impure commercial acid is made by heating pulverized phosphate rock with sulfuric acid: $Ca_3(PO_4)_2 + 3H_2SO_4 = 2H_3PO_4 + 3CaSO_4$. The greater portion of the calcium sulfate formed in the reaction is precipitated and separated by filtration. The acid is also manufactured by a method similar to the preparation of the free element by heating phosphate rock with carbon and sand, but differing in that air is introduced to oxidize the phosphorus vapor to the pentoxide, which is absorbed in water.

The most important salts of ortho-phosphoric acid are the calcium compounds. The occurrence of enormous deposits of the slightly soluble **tricalcium phosphate** has been mentioned. Soluble phosphate constitutes an important constituent of fertile soils and large quantities of phosphate rock (U. S. production about 3,500,000 tons yearly) are mined and converted into the soluble salt, $Ca(H_2PO_4)_2$, for use as fertilizer: $Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O = Ca(H_2PO_4)_2 + 2CaSO_4 \cdot 2H_2O$. The mixture of acid phosphate and gypsum is sold under the name of "**superphosphate of lime.**" It seems likely that **ammonium phosphate** will to a certain extent replace the superphosphate as a fertilizer (Par. 17).

Most of the normal orthophosphates are but slightly soluble. The compounds, **ammonium magnesium phosphate,** $MgNH_4PO_4 \cdot 6H_2O$, and **ammonium phosphomolybdate,** $(NH_4)_3PO_4 \cdot 12MoO_3$, are mentioned under analytical properties. **Microcosmic salt,**

$Na(NH_4)HPO_4$, is used in bead tests similar to the borax bead. The **disodium phosphate,** $Na_2HPO_4 \cdot 12H_2O$, is employed as a laboratory reagent. This compound loses water upon heating, forming several other hydrates, and finally at about 95°, the anhydrous salt.

If the ortho-acid is heated to 215°, water is lost and **pyrophosphoric acid** is formed: $2H_3PO_4 = H_4P_2O_7 + H_2O$. When this acid is dissolved in cold water, the rate of transformation back into the ortho-acid is slow, but the transformation is rapid in hot water. All four hydrogen ions are replaceable by metals, and the four ionization constants are: $k_1 = 1.4 \times 10^{-1}$, $k_2 = 1.1 \times 10^{-2}$, $k_3 = 2.9 \times 10^{-7}$, $k_4 = 3.6 \times 10^{-9}$. The silver salt, $Ag_4P_2O_7$, is but slightly soluble, and the magnesium salt, $Mg_2P_2O_7$, is of analytical importance. Sodium pyrophosphate is readily formed upon heating disodium hydrogen phosphate, Na_2HPO_4. The pyro-acid may be distinguished from the other phosphoric acids through the formation of a precipitate with zinc acetate.

Metaphosphoric acid, HPO_3, called glacial phosphoric acid is formed as a transparent glass by strongly igniting either the ortho- or pyro-acid. Like the pyro-acid, it is transformed but slowly into the ortho-acid in cold water. Most metaphosphates are insoluble, and the acid may be distinguished from the other phosphoric acids by the fact that it gives a precipitate with calcium ion.

55. The Peroxyphosphoric Acids.—H_3PO_5 and $H_4P_2O_8$ (compare Peroxysulfuric Acid), are formed by the electrolysis of solutions of the salt, K_2HPO_4, containing a little potassium fluoride and dichromate. The former is the principal product at high current density and the latter at lower current densities. The former may also be prepared by treating the pentoxide with cold 30 per cent hydrogen peroxide.

56. Oxides and Acids of Arsenic.—The **trioxide,** As_2O_3, (As_4O_6), generally known as **white arsenic** is commercially the most important compound of the element. Its most important source is the flue dust of smelters roasting arsenic-containing ores, and it is recovered from the dust by resubliming. The vapor condenses to a vitreous form which slowly changes to an octahedral crystalline modification. A monoclinic form may be prepared by heating for some time at 200°. The oxide is slightly

soluble in cold water and more soluble in hot water. The rate of solution in both cases is very slow. The solution contains **arsenious acid,** H_3AsO_3. About 60 per cent of the white arsenic consumed in the United States (75,000 tons per annum) is used in the manufacture of insecticides, and 25 per cent in the manufacture of glass. Smaller quantities are used in the preparation of ant paste and rodent poison, as a mordant in dyeing, and as a wood preservative. The fatal dose of the oxide is 0.06–0.2 g., but a toleration may be developed that will permit the consumption of several times this amount without harmful effects. A number of organic arsenic compounds are used in medicine, which are highly toxic to lower organisms, but which can be tolerated in fairly large quantities by the human body.

Although the trioxide is somewhat amphoteric, it is more acidic than basic and dissolves readily in alkalies forming **arsenites.** Salts of the types Na_3AsO_3, $NaAsO_2$, and $Na_2As_4O_7$ may be obtained, but the free poly-acids are not stable and decompose to give the oxide. The soluble salts are highly hydrolyzed, due to the weakness of the acid. Ferric and magnesium arsenites are very slightly soluble, and suspensions of the hydroxides of these ions are administered in cases of arsenic poisoning. A number of copper arsenites are important insecticides and pigments, such as **Paris green,** $Cu_4(C_2H_3O_2)(AsO_3)_2$, and **Scheele's green,** $CuHAsO_3$.

The trioxide dissolves in concentrated hydrochloric acid to form a **trichloride** but this compound is completely hydrolyzed in dilute acid solution.

Arsenious acid may be oxidized to arsenic acid:

$$H_3AsO_3 + H_2O = H_3AsO_4 + 2H^+ + 2E^-, \quad -0.49 \text{ volt.}$$

As is evident from the potential value, a fairly strong oxidizing agent is required. In neutral solution the reaction with iodine is quantitative, but in acid solution, the reaction is reversed and arsenic acid oxidizes iodide quantitatively. A value of -0.24 volt is given in Table XII for the metal-arsenite couple.

57. Orthoarsenic acid is obtained upon evaporating a solution made by dissolving the trioxide in nitric acid. It crystallizes as $2H_3AsO_4 \cdot H_2O$. When heated, water is lost to form the pentoxide, As_2O_5, which readily dissolves again in water to form the acid.

Arsenates resemble the phosphates in solubility and crystalline

form. The sodium salts, Na_2HAsO_4 and $Na_4As_2O_7$, are used in the preparation of the **lead arsenates,** $Pb_3(AsO_4)_2$ and $PbHAsO_4$, which are used extensively as insecticides. The value of arsenic as an oxidizing agent has been discussed above.

58. Oxides and Acids of Antimony.—The so-called **trioxide,** Sb_2O_3 (or Sb_4O_7), together with some tetroxide, is formed when antimony burns in air. The tetroxide may be prepared from the trioxide by heating in air to moderate temperature (300–400°), but at higher temperatures (about 900°) it decomposes again to the trioxide. The trioxide is amphoteric. It dissolves in concentrated acids, but only basic salts can ordinarily be crystallized from the solutions, e.g. $(SbO)_2SO_4$, $(SbO)NO_3$, and $K(SbO)$-$C_4H_4O_6$. In hot water, these salts are completely hydrolyzed. The basic radical, SbO, is known as **antimonyl,** and the potassium antimonyl tartrate has long been used in medicine under the name of **tartar emetic.** The antimonyl ion gives only a very small concentration of Sb^{+++}.

The trioxide dissolves in alkalies forming salts of **antimonous acid.** The sodium meta-antimonite, $NaSbO_2 \cdot 3H_2O$, may be crystallized from the solution in sodium hydroxide. Salts of the ortho- and pyro-acids are also known.

The **tetroxide** is acidic in properties, dissolving in alkalies, but not acids. Two **hypoantimonates** occur as minerals, $CaSb_2O_5$ and $CuSb_2O_5$.

Antimony pentoxide, like the corresponding oxide of arsenic, may be prepared by the action of nitric acid upon the trioxide, and hydrates corresponding to the ortho-, meta-, and pyro-acids are known. The oxide and acids are only slightly soluble in water but dissolve in alkalies. The potassium acid pyroantimonate, $K_2H_2Sb_2O_7$, is very soluble in water, but the corresponding sodium compound is the least soluble of all sodium salts, and is sometimes employed as a test for sodium. As the solubility is about 0.03 g. per liter, the test is not delicate. The acid is a good oxidizing agent:

$$H_3SbO_3 + H_2O = H_3SbO_4 + 2H^+ + 2E^-; \quad -0.75 \text{ volt.}$$

59. Bismuth Oxides, Hydroxides and Acids.—Bismuth monoxide is prepared by heating basic bismuth oxalate: $(BiO)_2C_2O_4 = 2BiO + 2CO_2$. It is readily oxidized to the **trioxide.** The latter oxide occurs in nature, and may be formed upon heating

the metal in air. It has a yellow color, a comparatively high melting point, and exists in several crystalline modifications. This oxide is not soluble in bases but dissolves in acids, and normal salts may be obtained by evaporating the acid solutions. When treated with water in the absence of acid, these salts are hydrolyzed to basic compounds, e.g. **basic nitrate,** $Bi(OH)_2NO_3$, **basic sulfate,** $(BiO)_2SO_4$, and **oxychloride,** BiOCl. A number of **basic carbonates** are known. These, and also the basic nitrate, are employed in medicine in the treatment of infections of the alimentary canal. The **hydroxide,** $Bi(OH)_3$, is precipitated from the salt solutions by alkalies. It is not soluble in excess of the reagent. Bismuth ion is readily reduced to the metal:

$$Bi = Bi^{+++} + 3E^-; \quad -0.2 \text{ volt.}$$

60. Bismuth pentoxide, Bi_2O_5, is formed by the action of very strong oxidizing agents upon the trioxide, e.g. NaClO in weakly alkaline solution. It is comparatively non-reactive. In concentrated sodium hydroxide it forms **sodium bismuthate,** $NaBiO_3$. In water or acid, this compound hydrolyzes to the acid, which is a very powerful oxidizing agent:

$$Bi^{+++} + 3H_2O = HBiO_3 + 5H^+ + 2E^-; \text{ ca } -1.7 \text{ volts.}$$

The acid will even oxidize manganous ion to permanganate in acid solution. Ortho-bismuthates are not known, although a tetroxide, Bi_2O_4, which is said to be formed along with the pentoxide by the action of chlorine in alkaline solution upon the trioxide, is considered to be bismuth orthobismuthate, $Bi(BiO_4)$.

61. Halogen Compounds.—The various halogen compounds are summarized below.

TABLE XVI

HALIDES OF PHOSPHORUS, ARSENIC, ANTIMONY AND BISMUTH
X = any halogen

P	As	Sb	Bi
			BiCl
PCl_2, PI_2	AsI_2		$BiCl_2$, $BiBr_2$
PX_3	AsX_3	SbX_3	BiX_3
		$SbCl_4$ in Rb_2SbCl_6	$BiCl_4$
PX_5 (except I)	AsF_5	SbX_5 (except I)	BiF_5

The halides may, in general, be prepared by the direct action

of the elements. The compounds, AsX_3, SbX_3, and BiX_3, may also be prepared by treating the corresponding oxide with the concentrated halogen acid. The relatively unstable PCl_2 is formed by passing an electric spark through mixtures of PCl_3 vapor and hydrogen.

The salt-like nature of the compounds increases with the increasing size of the elements of the group; thus phosphorus trichloride is a non-conductor of electricity, while molten bismuth trichloride conducts readily. The halides are hydrolyzed by water, e.g. $PCl_5 + 4H_2O = H_3PO_4 + 5HCl$. Often an oxyhalide forms as the first step, e.g. $POCl_3$, SbOCl, and BiOCl. The more basic the oxide, the less is the tendency of the halide toward hydrolysis: thus the hydrolysis of antimony and bismuth trichloride at ordinary temperatures stops at the oxychloride, and the reaction is readily reversed by acid. On account of its ready hydrolysis, phosphorus trichloride is used extensively in organic chemistry to replace hydroxide by chloride, e.g. $3CH_3CO \cdot OH + PCl_3 = 3CH_3COCl + H_3PO_3$. Antimony trichloride early received the name of **butter of antimony** and was employed for medicinal purposes. It was prepared by the reaction: $Sb_2S_3 + 3HgCl_2 = 3HgS + 2SbCl_3$. Bismuth triiodide is soluble in excess iodide, forming salts of the complex iodide BiI_4^-. The antimony tetrachloride is known only in complex salts.

62. Sulfides.—The following sulfides are known:

P	As	Sb	Bi
	AsS		BiS
P_4S_3			
P_2S_3	As_2S_3	Sb_2S_3	Bi_2S_3
		Sb_2S_4	
P_2S_5	As_2S_5	Sb_2S_5	
PS_6			

The **sulfides of phosphorus** may be prepared by heating together the elements in equivalent amounts. Only two of the compounds, P_2S_5 and P_4S_3, are sufficiently stable to be crystallized from solution in carbon disulfide. The pentasulfide is used as a reagent in organic chemistry. The trisulfide, P_4S_3, has been mentioned in connection with the manufacture of matches.

Arsenic monosulfide, AsS, occurs as the mineral realgar. It may be formed by heating together the elements, or by the reaction: $FeS_2 + FeSAs = 2FeS + AsS$. The yellow trisulfide, As_2S_3, also occurs as a mineral, **orpiment.** It is precipitated from solutions of arsenites by hydrogen sulfide. With pure arsenious acid, the precipitate is colloidal, but is coagulated by hydrogen ion or other positive ions. The sulfide is not soluble in concentrated hydrochloric acid. The sulfide is acidic in nature and dissolves in excess sulfide ion, forming **thioarsenite:** $As_2S_3 + 3S^{--} = 2AsS_3^{---}$. In polysulfide, it is oxidized to **thioarsenate:** $As_2S_3 + 2S_2^{=} + S^{=} = 2AsS_4^{---}$. The yellow trisulfide changes to a red form at 170°. The pentasulfide, As_2S_5, is formed by passing hydrogen sulfide into an acid solution of an arsenate. It is soluble in sulfide ion, forming the thioarsenate: $As_2S_5 + 3S^{--} = 2AsS_4^{---}$, and is reprecipitated from this compound by acid. The sulfide is not very stable and decomposes rather easily into the trisulfide and sulfur.

The mineral **stibnite,** Sb_2S_3, is black, but the antimony trisulfide, precipitated from solutions of the trichloride or antimonites, is orange red. It is soluble in concentrated hydrochloric acid, but not in dilute. It dissolves in sulfide and polysulfide, forming **thioantimonites** and **thioantimonates,** similar to arsenic trisulfide. When the thioantimonates are acidified, the **tetrasulfide** and sulfur are precipitated: $2SbS_4^{---} + 6H^+ = Sb_2S_4 + S + 3H_2S$. The tetrasulfide forms a mixture of thioantimonite and thioantimonate with excess sulfide ion, and is soluble in concentrated acid.

Black **bismuth sesquisulfide** is formed by heating together the element or by the action of hydrogen sulfide upon bismuth salts. It is not soluble in dilute hydrogen ion, but is dissolved by hot dilute nitric acid with the oxidation of the sulfur. It is not soluble in sulfide or polysulfide.

63. Metal Compounds.—Phosphides may be prepared (1) by heating together phosphorus and the finely divided metal or, (2) metal oxide; or by the action of (3) phosphorus, or (4) phosphine upon solutions of metal salts. Examples of (1) are Hg_3P_4, MnP_2, Sn_3P (used in phosphor bronze), K_2P_5, PbP_5; (2) Ca_3P_2; (3) Ag_3P, Cu_3P_2 and (4) Hg_3P_4, Cu_2P.

Arsenic unites with almost all metals at red heat, e.g. $CoAs_2$, $FeAs_2$, Fe_4As_3, NiAs, MnAs. Antimony forms a series of

compounds with an apparent valence number of − 2, e.g. CuSb, NiSb, ZnSb, $PtSb_2$; and also compounds with a valence number of − 3, e.g. Ag_3Sb, Mg_3Sb_2, Cd_3Sb_2, Fe_3Sb_2. Bismuth also forms a number of metal compounds, e.g. Mg_3Bi, although not so many as antimony.

Analytical

64. Phosphorus compounds are usually detected and determined as phosphate, since nitric acid readily oxidizes all of the lower valences to this ion. In the absence of heavy metals whose phosphates are insoluble in ammonia, the phosphates may be precipitated as magnesium ammonium phosphate, $MgNH_4PO_4$, by a solution of magnesium chloride, ammonium hydroxide and ammonium chloride. In quantitative determinations, this is ignited and weighed as $Mg_2P_2O_7$. Ordinarily the phosphate is precipitated in dilute nitric acid as the ammonium phosphomolybdate: $H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 = (NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4NO_3 + 12H_2O$. This precipitate is usually not weighed as such but is (1) dissolved in ammonium hydroxide and the phosphate reprecipitated as $MgNH_4PO_4$ or (2) titrated with standard hydroxide: $2(NH_4)_3PO_4 \cdot 12MoO_3 + 46OH^- = 2HPO_4^{--} + 6NH_4^+ + 24MoO_4^{--} + 22H_2O$.

Arsenic, antimony and bismuth are usually detected by precipitation as sulfides in dilute acid solution. The properties of these compounds have been discussed, and the systematic scheme of separation (Append. VI) should also be consulted for the outline of the analysis. Arsenic is sometimes determined quantitatively as the ammonium arsenomolybdate similar to phosphate given above. It is more often determined by the oxidation of arsenite to arsenate in the presence of bicarbonate by iodine. Antimony may likewise be determined by the oxidation of antimonite to antimonate by iodine in alkaline solution, or better by the reduction of antimonic acid by iodide in acid solution. Bismuth may be precipitated and weighed as the oxychloride, BiOCl, or precipitated as the hydroxide and weighed as the trioxide.

Small quantities of arsenic and antimony are determined by the **Marsh test,** in which arsine and stibine are formed by reduction with zinc in hydrochloric acid, and the mixture of the gases

with hydrogen passed into silver nitrate solution. Any antimony present is precipitated as silver antimonide, while the arsine is oxidized to arsenious acid. Upon filtering, the arsenic is confirmed in the filtrate by reprecipitration as sulfide, while the antimony in the precipitate is dissolved in hot concentrated tartaric acid and then reprecipitated as the sulfide. The test for arsenic may be modified by first separating the arsenic from the antimony by volatilizing the former as $AsCl_3$ from a hydrochloric acid solution, and then, after reduction with zinc, detecting the arsine by placing a strip of paper wet with copper sulfate solution in the stream of gas. From the depth of color of the copper arsenide formed on the paper, the quantity of arsenic may be estimated. The method is capable of detecting 0.001 milligram of arsenic.

CHAPTER XII

SULFUR, SELENIUM, AND TELLURIUM

1. The relation of the three elements, sulfur, selenium, and tellurium to oxygen has been discussed in Chapter **II.** The outstanding characteristics of these elements is the six valence electrons and the tendency to add two more electrons to complete the octet. Thus the members of the group all form compounds with the electropositive elements, in which they exhibit a valence of minus two, and with the more electronegative elements compounds with positive valence varying from one to six. The most important of their compounds are those with oxygen in which they have valences of $+4$ and $+6$. The elements are all solids with relatively low melting points. Sulfur is distinctly a non-metal, but selenium and tellurium, especially the latter, show certain metallic properties. A marked characteristic of the group is the existence of a number of allotropic modifications. In addition to these three elements, the extremely rare, unstable, and highly radioactive element, polonium, belongs to this group. The few known facts relating to its chemical behavior are given in Chapter **XXII.**

TABLE I

ATOMIC AND PHYSICAL PROPERTIES

	S	Se	Te
Atomic number	16	34	52
Atomic weight	32.06	79.2	127.5
Isotopes	none	74,76,78,80,82	126,128,130
Electrons in various quantum levels,			
1st	2	2	2
2d	8	8	8
3d	6	18	18
4th		6	18
5th			6
Density	R 2.07	G 4.80	6.24
	M 1.96	R 4.50	
Melting point, ° C	114.5	217	450
Boiling point, ° C	448.5	690	1390
Size of X^{--} in crystals, cm. $\times 10^8$			
(if $Cl^- = 1.81$)	1.84	1.98	2.21

2. Occurrence.—The amount of sulfur in the earth's crust is estimated at 0.1 per cent. Most of this occurs primarily as iron sulfide, but oxidation has given rise to large deposits of sulfate, chiefly of calcium and magnesium. The sulfides of all the heavy metals, except gold and platinum, occur as minerals, the most extensive deposits being those of iron pyrites, FeS_2. Free sulfur occurs in numerous deposits, of special importance being those in Louisiana and Texas, and in Sicily.

Selenium and tellurium are much less abundant than sulfur. The former occurs in the free state in most of the sulfur deposits, as selenides of many of the heavy metals, especially copper, silver and lead; and less frequently selenites of copper, lead, cobalt and other metals. Tellurium occurs chiefly as tellurides of copper, lead, silver, gold, iron, or bismuth. Tellurites and free tellurium are of rare occurrence.

The Free Elements

3. Sulfur.—Sulfur vapor at the boiling point has a molecular weight of 230 and is mostly S_8, with some S_6 and S_2. At 1000° it is largely S_2 and at 2000° is about half dissociated into atomic sulfur. This tendency of sulfur to form complexes is a common characteristic of the group and may be attributed to the readiness with which a sulfur atom, $\dot{\dot{S}}:$, will share its electrons with other sulfur atoms in an effort to complete the octet. Liquid sulfur contains two molecular species called S_λ and S_μ (probably S_8 and S_6), and possibly one or two others. At 120° the equilibrium liquid contains 3.6 per cent S_μ and at the boiling point 35 per cent. The heat of the transition is 416 calories. Such an equilibrium is probably not infrequent in liquids but the unusual feature with sulfur is the slowness with which the equilibrium state is reached. The time required is still further increased by the presence of traces of iodine or sulfuric acid, but is decreased by ammonia. Near the melting point sulfur is a light yellow mobile liquid; as the temperature is increased it becomes darker and more viscous with increasing content of S_μ. The viscosity reaches a maximum around 200°, and falls off rapidly as the boiling point is approached.

Solid sulfur exists in two crystalline forms, rhombic and monoclinic, Figure 1. There have been prepared, also, two

other monoclinic, one triclinic and one rhombohedral form, but they are unstable with respect to the common forms. There are also a number of amorphous and colloidal forms whose characteristics doubtless depend chiefly upon the degree of dispersion. Rhombic sulfur is in equilibrium with monoclinic at 96° C. The reaction is rather slow, however, and by rapidly cooling sulfur, held for some time just above its melting point, the long needle-shaped monoclinic crystals may be obtained. At room temperature they are transformed into rhombic in about a day. The heat of the transition is 70 cal. Rhombic sulfur melts at 112.8°, in equilibrium with S_λ, and at 110.4° to form the equilibrium mixture $S_{\lambda\mu}$. Monoclinic sulfur melts at 119.2° to form S_λ and 114.5 to form $S_{\lambda\mu}$. Both forms are soluble in CS_2. At 25° the solubility of the monoclinic is 1.28 times that of the rhombic. The molecular form of the solute in both cases is S_8. By heating sulfur near its boiling point, and suddenly cooling, a very plastic substance is obtained which consists of a mixture of rhombic crystals and an amorphous form not soluble in carbon disulfide. The latter form is essentially the super-cooled liquid. After some time it becomes very hard. The rate of change of the amorphous into the rhombic form requires years at ordinary temperature, but is rapid at 100°. There is at least one other amorphous modification, this form being soluble in carbon bisulfide. Finely divided sulfur prepared by precipitating sulfur from calcium polysulfide by the

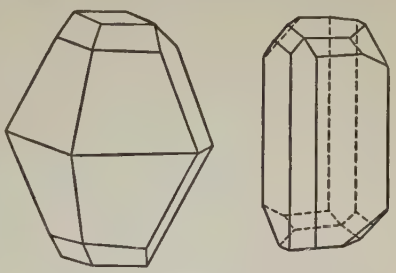


FIG. 1.—Crystal forms of sulfur; sulfur rhombic (left) and sulfur monoclinic (right).

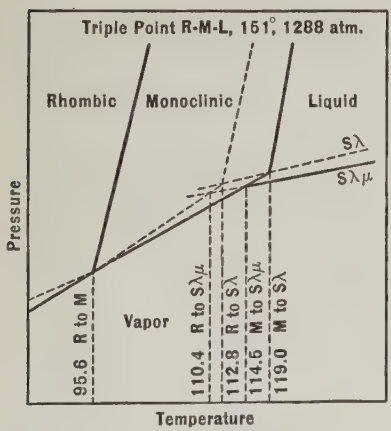


FIG. 2.—Pressure-temperature diagram for sulfur; diagrammatic as actual vapor pressures are not known.

addition of acid is known as **milk of sulfur,** and finely divided sulfur formed by sublimation is known as **flowers of sulfur.**

The various forms of sulfur are all non-conductors of electricity and are insoluble in water.

4. The salt domes of Louisiana and Texas have now supplanted the mines of Sicily as the world's most important source of sulfur. These enormous domes consist of a salt core covered with a cap of gypsum, dolomite, and limestone in which the sulfur occurs. It is extracted by the ingenious Frasch Process. Water heated to about 180° under pressure is pumped down bore holes and forced into the deposits; the sulfur is liquefied, and when a quantity of it collects at the bottom of the cavity it is forced to the surface by an air lift and discharged into bins. A small amount of sulfur is obtained from the purification of illuminating gas (Par. 8). The production of sulfur in the United States in 1926 was 1,850,000 tons. The major portion of this is made into sulfuric acid. Smaller amounts are consumed in the vulcanization of rubber, in the manufacture of sulfites and thiosulfates, in bleaching dried fruit, and for dusting and spraying plants.

5. Selenium.—Selenium vapor at the boiling point consists of mixtures of $Se_8 - Se_2$. The liquid also doubtless contains a number of molecular complexes but the problem has not been carefully investigated. The solid exists in three crystalline modifications, two of them rather similar monoclinic forms, red in color, soluble in carbon disulfide and unstable with respect to the third form, a hexagonal rhombohedral structure known as metallic or grey selenium. The monoclinic forms are relatively stable below 100° and melt somewhat below 200°, the exact temperature being in doubt due to their rapid transformation, upon heating, into the grey form. The latter form melts at 220° and is insoluble in carbon bisulfide. Like sulfur, there is an amorphous modification, vitreous and black in color, which may be prepared by quickly cooling the liquid. Reduction of selenates results in the formation of two red modifications, one crystalline and the other amorphous. A number of colloidal forms of selenium have been prepared.

The electrical conductivity of the grey form is poor, but is greatly increased by light. This property makes selenium useful in the construction of apparatus for the measurement of light

intensity, as in photometers for measuring the intensity of radiation coming from the stars, and for the automatic turning of lights on and off at night and morning, respectively.

Large quantities of selenium could be recovered from the flues of the sulfur burners in sulfuric acid plants, and from the anode mud of electrolytic copper refineries. The free element has no extensive commercial applications. The largest consumption is in the glass works for making ruby red glass, and to neutralize the green color of glass, due to the presence of ferrous silicate

6. Tellurium.—The vapor of tellurium at the boiling point contains a much smaller per cent of the higher molecular complexes than in the case of sulfur and selenium, being mostly Te_2. The solid crystallizes in a silver white, semi-metallic, rhombohedral form, isomorphic with grey selenium, and in a second modification as yet little known. It may be precipitated in an amorphous modification by reduction and like the other members of the group readily forms various colloidal solutions. The amorphous form changes to the crystalline extremely slowly at ordinary temperatures, but rapidly just below the melting point. The metallic modification is insoluble in carbon bisulfide. Its density is 6.24. It is the poorest electrical conductor of any of the metals, specific resistivity being 2×10^{-1} ohm-cm. Tellurium with an atomic number of 52 has a higher atomic weight than iodine, atomic number 53. This situation arises through a preponderance of the heavier isotopes of tellurium. Fairly large quantities of tellurium could be recovered from a number of metallurgical processes, especially the electrolytic copper refineries. Tellurium has been known as the useless metal. It is employed in a limited way in the ceramic industries.

7. Hydrogen Compounds.—The compounds, H_2S, H_2Se, H_2Te, are much less polar liquids than water, as is indicated by their lower melting and boiling points. Their stability decreases and their power as reducing agents (Table II) increases with increasing atomic weight; that is, with increasing size of the atom, it becomes easier to pull off the two extra electrons. Hydrogen selenide and hydrogen telluride are endothermic. These compounds all possess very disagreeable odors and are extremely toxic.

TABLE II

HYDROGEN COMPOUNDS OF SULFUR GROUP

	H_2S	H_2Se	H_2Te
Melting point, ° C.	− 83	− 64	− 48
Boiling point, ° C.	− 60	− 42	− 2
Heat of formation $H_2 + X = H_2X$ (gas); Kg. cal.	4.8	− 25	− 35
Reduction potential H_2X (gas) $= X + 2H^+ + 2E^-$, in volts	− 0.17	+ 0.4	+ 0.7

8. Hydrogen Sulfide.—Hydrogen sulfide may be formed by passing hydrogen into boiling sulfur, but is usually prepared by the action of acid upon a sulfide, particularly ferrous sulfide: $FeS + 2H^+ = Fe^{++} + H_2S$. The gas is soluble in water at 20° and 1 atmos. to the extent of 290 volumes per 100 volumes of water. In solution, it behaves as an extremely weak dibasic acid; the first ionization constant, $H_2S = H^+ + HS^-$, is about 9×10^{-8}, and the second ionization constant, $HS^- = H^+ + S^{--}$, about 10^{-14}. The soluble sulfides are, accordingly, highly hydrolyzed, $0.1N$ Na_2S containing about $0.085N$ OH^-. The acid sulfides or hydrosulfides, such as NaSH, are much less alkaline; $0.1N$ NaSH contains $0.001N$ OH^-.

The sulfides of nearly all the metals except those of the main groups I, II, and III are insoluble in water. Extensive use is made in quantitative analysis of the varying degrees of solubility of the sulfides. Due to the weakness of hydrogen sulfide, the solubility of all sulfides is increased in acid. However, certain of the sulfides are so extremely insoluble that even large concentrations of hydrogen ion do not increase the solubility sufficiently to dissolve them in appreciable amounts. In general practice the metal sulfides are divided into two groups: (1) those precipitated in $0.3N$ H^+ by H_2S, and (2) those not precipitated under these conditions. For details of the classification and separation, reference may be made to the general scheme of analysis, Appendix VI (cf. Hildebrand, *Prin. of Chem.*, p. 199).

Hydrogen sulfide burns in excess of air to form sulfur dioxide and water. In a limited amount of air, the free element is formed, as the dioxide and hydrogen sulfide react according to the equation: $2H_2S + SO_2 = 3S + 2H_2O$. Advantage is taken

of the oxidation in a limited quantity of air to remove hydrogen sulfide from illuminating gas, where it is objectionable because of its odor and the corrosive nature of its combustion products, the process being carried out by admitting a small amount of oxygen and heating the mixture. The sulfur precipitated by the reaction is sold as a by-product.

Hydrogen sulfide tarnishes the surface of even such a noble metal as silver: $2Ag + H_2S = Ag_2S + H_2$. The action of hydrogen sulfide here as an oxidizing agent with the liberation of hydrogen is, of course, due to the great stability of silver sulfide. The absorption of sulfur by the alkaline sulfides is discussed under the polysulfides.

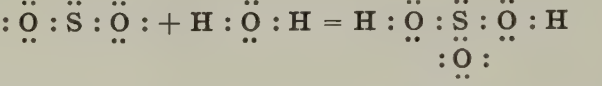
9. Hydrogen Selenide and Telluride.—The direct combination of hydrogen with selenium and tellurium shows less tendency to take place than with sulfur: however, the reactions do proceed to some extent at high temperatures. The compounds can be prepared, respectively, by the action of acid upon iron selenide or upon magnesium or aluminum telluride. They are gases with very disagreeable odors, and dissolve in water to form dibasic acids, probably slightly stronger than hydrogen sulfide. The selenides and tellurides of the heavy non-alkali metals are insoluble in water. The combustion reactions of these compounds are similar to hydrogen sulfide, but take place with greater energy (Table II). Hydrogen telluride decomposes rapidly above 0°.

10. Oxides.—Sulfur forms the oxides S_2O_3, SO_2, SO_3, and S_2O_7; selenium only SeO_2; and tellurium TeO, TeO_2, and TeO_3. The slight tendency of selenium to form oxides is interesting in connection with the same characteristic of bromine, which occupies a position but one atomic number higher than selenium (cf. **XII—40**). The heat of formation of selenium dioxide is also less than either of the others, the values in kg. cals. being: SO_2(gas) 71, SeO_2(solid) 57, and TeO_2(solid) 87.

11. Sulfur Sesquioxide.—Sulfur reacts with concentrated sulfuric acid or with the trioxide to form the unstable solid sesquioxide, S_2O_3. It is not an acid anhydride, although its valence corresponds to the hyposulfurous acid, $H_2S_2O_4$.

12. Sulfur Dioxide and Sulfurous Acid.—Sulfur dioxide is a gas condensing to a liquid at $-10°$. It is formed by the oxidation of sulfur or sulfides, and by the reduction of sulfuric acid:

$S + O_2 = SO_2$; $4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$; $2H_2SO_4 + Cu = CuSO_4 + SO_2 + 2H_2O$. Due to the instability of sulfurous acid, the gas is liberated by the action of strong acids upon sulfites: $Na_2SO_3 + H_2SO_4 = Na_2SO_4 + SO_2 + H_2O$. The gas is, however, moderately soluble in water, 50 volumes per unit volume of water at 20° and 1 atmosphere, forming sulfurous acid in solution. In terms of the electron structures, this reaction is:



Sulfurous acid is a rather weak dibasic acid, somewhat resembling carbonic acid. Its first ionization constant is 0.017 and the second 5×10^{-6}. Sulfurous acid is a fair oxidizing agent (Table III). It is unstable with respect to the decomposition: $3H_2SO_3 = 2SO_4^{--} + 4H^+ + S + H_2O$; 0.33 volt. This reaction is slow but takes place under the influence of violet light and upon heating. Its most important reaction, however, is its oxidation to sulfuric acid (Table III). Many of its industrial uses depend upon this action as a reducing agent.

TABLE III

Oxidation-Reduction Potentials of Sulfurous and Sulfuric Acids

	Volts$_{25°}$
$S + 3H_2O = H_2SO_3 + 4H^+ + 4E^-$	− 0.47
$H_2SO_3 + H_2O = SO_4^{--} + 4H^+ + 2E^-$	− 0.14

The alkali sulfites are but slightly hydrolyzed. The sulfites of many of the heavy metals are insoluble. The acid sulfites occur in two types, such as $NaHSO_3$ and $Na_2S_2O_5$, the latter being the anhydride of the former: $2HSO_3^- = S_2O_5^{--} + H_2O$.

At 20°, sulfur dioxide may be liquefied by a pressure of about 3 atmospheres. Because of its ease of liquefaction it is employed in refrigeration processes. The commercial product is usually sold as the liquid, in metal cylinders. Sulfurous acid has a powerful toxic action upon vegetable organisms, and thus finds many applications as a fungicide and as a preservative in the preparation of beverages and foods. Sulfurous acid and sulfites are used extensively as bleaching agents for silk and woolen textiles, straw hats, feathers, and dried fruits. Sulfites have a digesting action upon wood, tending to separate the fibers as

well as bleaching them, and their largest use is probably in the pulp and paper industry. Sulfur dioxide is also employed in petroleum refining.

13. Selenium Dioxide and Selenites.—The same general methods of preparing sulfur dioxide are applicable to selenium dioxide. This dioxide is a solid which sublimes without melting. It has a characteristic odor which is described as that of "rotten horse-radish." It dissolves in water to form weak selenious acid, H_2SeO_3. Upon evaporating the solution, the free acid separates, and upon further heating, decomposes to the oxide. The acid is a much more powerful oxidizing agent than sulfurous acid:

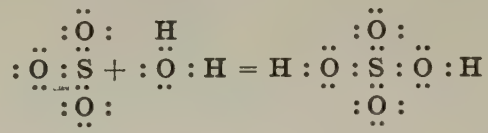
$$3H_2O + Se = H_2SeO_3 + 2H^+ + 2E^-, \text{ about } -0.7 \text{ volt.}$$

It thus oxidizes sulfurous acid to sulfuric: $2H_2SO_3 + H_2SeO_3 = 2H^+ + SO_4^{--} + Se + H_2O$. The selenium first separates as a red transparent colloid. When a solution of selenious acid is boiled with hydrogen bromide, the volatile tetrabromide escapes. Some attempts have been made to use the selenites as insecticides in fruit orchards, but they are so extremely toxic that they damage the growing plants.

14. Tellurium Dioxide and Tellurites.—Tellurium burns more readily than does selenium to form the dioxide. The dioxide is also formed by the action of other strong oxidizing agents upon the metal, and by reduction of tellurates. It does not unite readily with water but may be dissolved in alkali to form tellurites from which the slightly soluble acid may be obtained, upon acidifying, as a white solid. The acid may also be obtained by the oxidation of tellurium by nitric acid. The acid is somewhat amphoteric, forming salts of the "**telluryl**" radical, TeO^{++}, or even $Te_4O_7^{++}$, and with hydrogen iodide it forms the slightly soluble iodide, TeI_4. The acid forms a number of acid complexes of the general formula, $H_2TeO_3 \cdot nTeO_2$. It is a fair oxidizing agent but not so strong as selenous acid. It is not easily oxidized to telluric acid. The dioxide forms, upon heating with tellurium, the **monoxide**, TeO. This oxide may also be formed by the hydrolysis of the chloride, $TeCl_2$.

15. Sulfur Trioxide and Sulfuric Acid.—Sulfur trioxide, SO_3, is a colorless liquid, freezing at 15° and boiling at 46°. The solid soon changes from a transparent glassy form to the polymer,

S_2O_6, an opaque mass of needle shaped crystals which can be sublimed without melting. The trioxide possesses a remarkable affinity for water, forming sulfuric acid:



This reaction takes place with a hissing sound resulting from the large quantity of heat evolved, 38 kg. cal. The trioxide dissolves in concentrated sulfuric acid forming the bi- or pyro-sulfuric acid, $H_2S_2O_7$, called "fuming sulfuric acid" or "oleum."

16. Contact Process.—Sulfur trioxide is formed by the action action of oxygen (air) or other powerful oxidizing agents upon sulfur dioxide. The reaction, $SO_2 + \frac{1}{2}O_2 = SO_3$, has, at 25° and partial pressures of 1 atm., a potential of 0.35 volt. Like many direct oxidations by O_2, this reaction is extremely slow. However, the rate can be increased by certain surface catalysts, including ferric oxide and metallic platinum, the latter being most effective. This catalysis is the basis for the "contact process" for the manufacture of sulfuric acid. The efficiency of platinum as a catalyst increases with temperature, reaching a maximum about 500°, but the per cent of trioxide formed at equilibrium decreases at high temperature (Table IV).

TABLE IV

EQUILIBRIUM CONSTANTS FOR THE REACTION, $SO_2 + \frac{1}{2}O_2 = SO_3$

t ° C.....	300	527	680	790	900
K.....	8×10^3	28	3.6	1	0.38

The reaction is generally carried out between 380 and 450° with excess air, under which conditions 97 to 99 per cent of the dioxide is converted into trioxide. The efficiency of the catalyst depends upon the extent of active surface. The platinum is obtained in a finely divided state by heating chlorplatinic acid, H_2PtCl_6, and is dispersed upon a base of asbestos fibers, magnesium sulfate, or silica gel.

One of the factors in the successful operation of the process is the removal from the sulfur dioxide of all impurities which may

"poison" the catalyst and render it inactive. It is particularly important to remove traces of solid sulfur, selenium dioxide, mercury, and compounds of phosphorus and arsenic. The sulfur trioxide formed by the reaction is more readily absorbed from the excess of oxygen by concentrated sulfuric acid than by water. The discovery of this curious fact aided materially in the development of the process. The explanation appears to be in the formation of a fog through the absorption of water vapor by the sulfur trioxide when water is used as the absorbing medium. The fog particles are small drops of sulfuric acid, and their thermal motion, compared with gas molecules, is very slow. With concentrated sulfuric acid, no fog is formed, and the rapidly moving sulfur trioxide molecules are more readily absorbed when the gas is bubbled through the acid. As the trioxide dissolves, water is added to keep the acid at any desired concentration, usually at about 98 per cent acid. One of the mechanical problems is the temperature control. Since the reaction liberates heat, the temperature is kept from becoming too high by means of heat interchange between the incoming and outgoing gases. The reaction is carried out in cast iron containers, iron being insoluble (passive) in concentrated sulfuric acid.

17. Lead Chamber Process.—Many industries employ dilute sulfuric acid of no high degree of purity. It is cheaper to make this type of acid by the action of oxygen and steam upon sulfur dioxide, using nitric oxide as a catalyst. This process is known as the lead chamber process, from the large lead-lined reaction chambers employed. The presence of steam increases the ease of oxidation of sulfur dioxide, $SO_2 + O_2 + H_2O = H_2SO_4$, 1.1 volts at 25° C., as compared to 0.35 volts for the oxides. Although the various steps involved in the action of the gases with the catalyst are apparently quite complicated, the net result is that the nitric oxide acts as an oxygen carrier:

$$NO + \tfrac{1}{2}O_2 = NO_2$$
$$NO_2 + SO_2 + H_2O = NO + H_2SO_4$$

The reaction is carried out in immense lead chambers of approximately 200,000 cu. ft. capacity. The sulfuric acid condenses and is drained off at the bottom of the chamber. The nitrogen dioxide is recovered by passing the gas coming from the lead

chamber through concentrated sulfuric acid. The probable reaction is: $2NO_2 + H_2SO_4 = SO_2(OH)(NO_2) + HNO_3$. This reaction is reversed upon dilution; the nitric and nitrosyl sulfuric acid, $SO_2(OH)(NO_2)$, again forming sulfuric acid and nitrogen dioxide. Advantage is taken of this reversal to restore the oxides of nitrogen to the system by diluting the nitrogen containing acid, and by passing the sulfur dioxide, which also aids in the reversal by removing NO_2, through the solution before entering the lead chambers. This is carried out in a large tower employing the counter current principle. Thus the nitrogen oxides are again restored to the chambers and at the same time the chamber acid is concentrated. The ordinary chamber acid is about 60 to 70 per cent sulfuric acid and large quantities are sold at these concentrations. Further concentration may be carried out by evaporating in lead pans until a concentration of 77 per cent is reached. Below this concentration the lead is not rapidly oxidized because of a protective layer of sulfate. Above this concentration, however, the sulfate is soluble, and the concentration process is usually continued in iron vessels. The use of silica and silicon iron containers for the further concentration is becoming more general.

Formerly a large fraction of the sulfur dioxide consumed in the manufacture of sulfuric acid in this country was made by roasting iron pyrites, FeS_2, but at present the major portion is made by burning sulfur. Some sulfur dioxide is utilized from the stacks of the copper, zinc, and lead smelters.

18. Properties of Sulfuric Acid.—The specific gravity of sulfuric acid solutions increases rapidly with concentration becoming 1.85 for 100 per cent acid. The pure acid melts at 10.5°, but the melting point is greatly lowered by the presence of either water or sulfur trioxide. The boiling point is 270° at 755 mm., but is without special significance since the solution loses sulfur trioxide and changes in composition until the constant boiling mixture of 98.3 per cent sulfuric acid is reached at 338°. In addition to the compounds, $SO_3 \cdot H_2O$, (H_2SO_4) and $SO_3 \cdot H_2O$, $(H_2S_2O_7)$, the freezing point curves, Figure 3, indicate the hydrates, $SO_3 \cdot 2H_2O$, $SO_3 \cdot 3H_2O$, and $SO_3 \cdot 5H_2O$. The great stability of these hydrates renders sulfuric acid an excellent dehydrating agent. The concentrated acid will remove water from cellulose, $(C_6H_{10}O_5)_n$, and sugar, $C_{12}H_{22}O_{11}$, depositing

carbon: $C_{12}H_{22}O_{11} = 12C + 11H_2O$. It, however, is not as powerful a dehydrating agent as phosphorus pentoxide, since this oxide will liberate sulfur trioxide from sulfuric acid: $P_2O_5 + H_2SO_4 = 2HPO_3 + SO_3$. The heat of solution of sulfuric acid in a large amount of water is 19.0 kg. cal. Sulfuric acid is dibasic, the first ionization is fairly complete even at moderate concentration, although the activity of the ions is not as high as in the hydrochloric acid. The second ionization is considerably weaker, the constant being 0.011 at 25° C. At molal concentrations the potential of the acid as an oxidizing agent is not very great (Table III), but the energy of concentration is so large that the oxidizing power of the concentrated acid becomes very strong, sufficient to dissolve copper or silver.

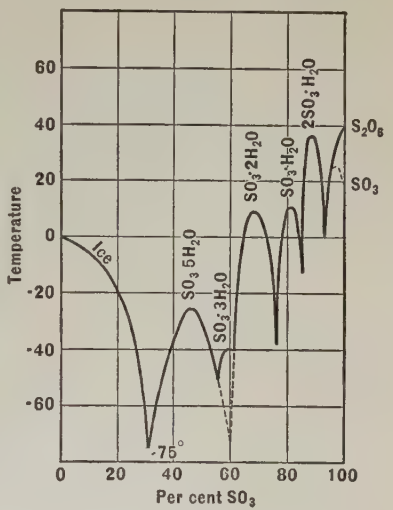


FIG. 3.—The system sulfur trioxide and water.

19. Applications of Sulfuric Acid.—The production of sulfuric acid in the United States in 1926 was over seven million tons of 62 per cent acid. The distribution of this acid among the more important consuming industries is given in Table V. Sulfuric

TABLE V

CONSUMPTION OF SULFURIC ACID IN U. S. IN 1926.

	TONS OF 62% ACID
Phosphate fertilizer	1,850,000
Petroleum	1,500,000
Iron and steel	750,000
Storage batteries and metallurgy	725,000
Ammonium sulfate	700,000
Chemicals	550,000
Paint	200,000
Explosives	190,000
Textiles	120,000

acid has played a leading role in the industrial development of the past century, due to its low cost of production and various useful chemical properties. The **high boiling point** accounts for its use in displacing more volatile acids such as hydrochloric, hydrofluoric, and nitric acids from their salts. As a **strong acid,** it is used to convert calcium phosphate to acid phosphate for fertilizer, to dissolve base metals and oxides, to clean metal surfaces prior to galvanizing and tinning, and to neutralize ammonia in its recovery from coke ovens and the packing industries. As a **dehydrating agent,** it plays an essential role in the manufacture of explosives, celluloid, pyroxaline, varnishes, ether, etc. The nitration process liberates water which is removed by the sulfuric acid thus allowing the reaction to go to completion. Many of its applications depend upon the **oxidizing power** of the concentrated acid, e.g. in removing tars and organic sulfides from petroleum. The **insolubility of many sulfates** is another factor of industrial importance, as in the manufacture of the important pigment, lithophone, a mixture of barium sulfate and zinc sulfide.

Pyrosulfuric acid, $H_2S_2O_7$, is used when the acid in its most powerful oxidizing and dehydrating form is desired. It was employed during the Great War to form "smoke screens," since it forms a very stable mist or fog composed of tiny drops of sulfuric acid.

20. Sulfates.—As a dibasic acid, sulfuric acid forms both neutral and acid salts. The acid salts may be dehydrated to form the pyrosulfates: $2NaHSO_4 = Na_2S_2O_7 + H_2O$. The normal salts of the alkali and alkaline earth metals and lead do not readily decompose upon heating, but the sulfates of the nobler metals evolve sulfur trioxide, or sulfur dioxide and oxygen if the decomposition temperature is high. The decomposition of ferric sulfate was once an important method of preparing sulfur trioxide and sulfuric acid. Sulfates are reduced by heating with carbon to form the sulfide: $Na_2SO_4 + 2C = Na_2S + CO_2$. Barium and lead sulfates are among the more important insoluble sulfates (Par. 32). Though insoluble in dilute acids, their solubility is increased in concentrated sulfuric acid by the slight weakness of the HSO_4^- ion.

21. Selenic Acid.—Rather powerful oxidizing agents, such as

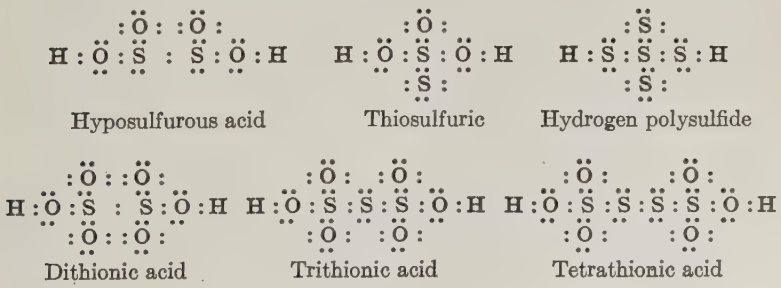
PbO_2 or Cl_2, are required to oxidize selenous to selenic acid, even in dilute solution:

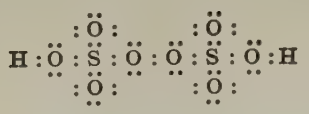
$$H_2O + H_2SeO_3 = H_2SeO_4 + 2H^+ + 2E^-, \; -1.1 \text{ volts.}$$

Conversely, selenic acid, when concentrated, is a very powerful oxidizing agent, liberating chlorine from chloride, and dissolving gold, but not platinum unless chloride is present. The reaction is, however, slow with many reducing agents, e.g. H_2S and SO_2, but is faster in the presence of chloride. The free acid is easily prepared by the action of bromine upon silver selenite: $AgSeO_3 + H_2O + Br_2 = H_2SeO_4 + 2AgBr$. The pure acid melts at 58° and its concentrated solution is thick and sirupy. When dehydrated, it gives selenous oxide and oxygen. The solubilities of the selenates are similar to the sulfates. The barium salt is easily confused with barium sulfate. The soluble selenates are, however, easily distinguished from sulfates by their higher oxidizing power.

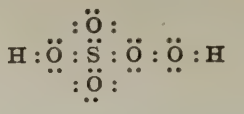
22. Tellurium Trioxide and Telluric Acid.—Telluric acid forms salts of the types Ag_6TeO_6 and Ag_2TeO_4. The acid, H_6TeO_6, is but sparingly soluble in water, and is but weakly acidic. Upon heating, it loses water to form H_2TeO_4 and then TeO_3. The trioxide does not react with water. Oxidizing agents with a potential of about 1.4 volts are required to oxidize tellurous acid to telluric, and it is therefore a powerful oxidizing agent itself. The ability of tellurium to hold more than the customary four oxygen atoms, as is shown in H_6TeO_6, is interesting in connection with the same property of iodine, which occupies the neighboring position in the periodic table.

23. Other Sulfur Acids.—A very large number of complex acids of sulfur exist,





Peroxydisulfuric acid



Peroxymonosulfuric acid

due to the ability of the sulfur atom to share electrons with oxygen and with other sulfur atoms, as is illustrated by the structural formulas of a number of these acids given above. The behavior of sulfur is somewhat comparable to carbon in this tendency to form molecules of high molecular weight with oxygen and hydrogen. A few of the more important acids will be discussed.

24. Hyposulfurous Acid.—The zinc salt of hyposulfurous acid is formed by the reduction of sulfurous acid by zinc: $2H_2SO_3 + Zn = ZnS_2O_4 + 2H_2O$. A solution of the sodium salt is prepared commercially from the zinc salt by the addition of sodium sulfite, as zinc sulfite is but moderately soluble. The salts are also prepared by the cathode reduction of sulfurous acid: $2H_2SO_3 + 2E^- = S_2O_4^{--} + 2H_2O$. The acid is too unstable to be prepared in the pure state. It is a very rapid reducing agent, reducing oxygen almost instantaneously. The sodium salt is employed commercially for the reduction of indigo to indigo white.

25. Thiosulfuric Acid.—Sulfites are reduced by sulfur in alkaline solution to thiosulfate: $SO_3^{--} + S = S_2O_3^{--}$. The free acid is unstable and the reaction is reversed by acid, sulfurous acid being formed and the sulfur precipitated. The reversal may be brought about even by weak acids: thus a sodium thiosulfate solution becomes turbid if exposed to the action of the carbonic acid of the air. The sulfur precipitated is amorphous and at first usually colloidal. The somewhat analogous oxidation of sulfide by sulfur in alkaline solution is discussed under the polysulfides. The product of that oxidation, SS_4^{--}, may be considered as the tetrathiosulfate.

Thiosulfate is oxidized by iodine, ferric ion, and other moderately strong oxidizing agents to the tetrathionate. This extremely important reaction with iodine is discussed under that element (cf. **X—21**). More powerful oxidizing agents, such as chlorine and bromine, oxidize the thiosulfate to sulfate: $5H_2O + S_2O_3^{--} + 4Cl_2 = 2SO_4^{--} + 8Cl^- + 10H^+$. Thiosulfate

forms complex ions and salts with many of the ions of the more noble metals, including Ag^+, Au^{+++}, Cu^+, Hg^{++}, Pb^{++}. Advantage is taken of this property in photography in the "fixing bath," to dissolve out the unchanged silver bromide.

Sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$, called "**hypo**" from the older name "hyposulfite," is of considerable commercial importance. Besides its use in photography, it is employed in the textile and paper industries as an "antichlor" to remove the excess chlorine used in bleaching, and in certain metallurgical processes.

26. Polysulfides.—Soluble sulfides readily dissolve sulfur to form a series of compounds giving the ions, S_2^{--} to S_5^{--}. The alkaline solutions may be evaporated and the crystalline salts obtained, but the acids are unstable, forming hydrogen sulfide and free sulfur. These polysulfides act both as reducing and oxidizing agents. An example of the latter action is the oxidation of stannous sulfide to thiostannate. Calcium polysulfide, made by dissolving sulfur in lime, the product thereby containing some thionic salts, is used extensively as an insecticide for vineyards and orchards.

27. Thionic Acids.—The structural formulas of a number of acids of the type, $H_2S_nO_6$, have been indicated above. The subscript varies from 2 to 5. These acids are analogous to the peroxyacids. Thus tetrathionic acid may be prepared by the anodic oxidation of thiosulfate, $2HS_2O_3^- = H_2S_4O_6 + 2E^-$, similarly to the preparation of peroxydisulfuric acid, $H_2S_2O_8$, from sulfuric acid; and the structure of the tetrathionate differs from that of persulfate only by the substitution of sulfur for the peroxygen. Mixtures of the acids result from the interaction of sulfurous and hydrosulfuric acid in solution: $H_2S + 3SO_2 = H_2S_4O_6$; $2H_2S + 6SO_2 = H_2S_3O_6 + H_2S_5O_6$; $3H_2S + 9SO_2 = H_2S_2O_6 + 2H_2S_5O_6$. The gases themselves react to form sulfur and water. The various acids or salts are formed as intermediate products in many oxidation-reduction reactions involving sulfates and sulfites: thus, manganese dioxide reacts upon cold sulfurous acid to form manganese dithionate: $MnO_2 + 2H_2SO_3 = MnS_2O_6 + 2H_2O$. The acids are unstable in regard to decompositions giving sulfate, sulfite, and sulfur. The tetrathionate is the most important of these compounds. Its formation from thiosulfate by the action of iodine and ferric ion has been discussed.

28. Peroxysulfuric Acid.—Two important acids and an oxide of sulfur containing peroxyoxygen are known. The oxide, S_2O_7, is formed in small amounts by an electrical discharge in a mixture of sulfur dioxide and oxygen: $2SO_2 + 3O_2 = 2S_2O_7$. It dissolves in sulfuric acid to form peroxydisulfuric acid, $H_2S_2O_8$. This acid, usually called persulfuric acid, may be prepared by the reaction between cold concentrated sulfuric acid and concentrated hydrogen peroxide: $2H_2SO_4 + H_2O_2 = H_2S_2O_8 + 2H_2O$, or by the electrolysis of cold concentrated sulfuric acid: $2HSO_4^- = H_2S_2O_8 + 2E^-$. The sodium salt is prepared commercially by the electrolysis of concentrated solution of sodium acid sulfate. The sodium peroxydisulfate is but moderately soluble and crystallizes out. Peroxydisulfuric acid hydrolyzes in steps forming first the peroxymono-acid called "**Caro's acid,**" and this hydrolyzes to form sulfuric acid and hydrogen peroxide: $H_2S_2O_8 + H_2O = H_2SO_4 + H_2SO_5$; $H_2SO_5 + H_2O = H_2SO_4 + H_2O_2$. The mono-acid may be prepared by the electrolysis of cold moderately concentrated sulfuric acid. Both of the acids evolve oxygen readily, but their salts are fairly stable. The sodium peroxydisulfate is of considerable commercial importance as an oxidizing agent:

$$2SO_4^{--} + 2H^+ = H_2S_2O_8 + 2E^-, \text{ about } -1.5 \text{ volts.}$$

In the presence of silver as a catalyst, manganous ion is oxidized to permanganate by the acid.

29. Other Thio-acids.—Sulfur may be substituted for oxygen in a number of acid radicals similar to its substitution in the sulfate radical, provided the radical is not such a powerful oxidizing agent that the sulfur is rapidly oxidized to higher valences. For example, compounds are prepared in which the oxygen in phosphate is replaced by sulfur, forming the series, Na_3PO_3S to Na_3PS_4. The strong analogy between sulfur and oxygen is well illustrated by the reaction of barium sulfide and carbon disulfide to give barium thiocarbonate, $BaS + CS_2 = BaCS_3$, similar to the formation of barium carbonate from the two oxides. Mention should also be made of **thiocyanic acid,** HCNS, as many of the salts of that acid are of considerable importance (cf. **XIII—26**).

30. Other Acids of Selenium and Tellurium.—The tendency to form long chain complicated acids, and the tendency to

substitute for oxygen, exhibited by sulfur in the thio-acids, decrease with the heavier elements in the group. Both selenium and tellurium form salts of polyhydro acids, e.g. $NaSe_2$, $NaTe_3$. Selenium forms an unstable peroxy-acid but tellurium does not. Selenium substitutes for oxygen in a number of acids and in many organic compounds, e.g. NaCNSe, sodium seleno-cyanate.

31. Halogen Compounds.—The halogens combine with the elements sulfur, selenium, and tellurium to form numerous compounds. These, together with a number of oxychlorides, compounds containing chlorine with oxygen and hydrogen, have been tabulated below:

S	Se	Te
SF_6	SeF_6 SeF_4	TeF_6 TeF_4
SCl_4 SCl_2 S_2Cl_2	$SeCl_4$ Se_2Cl_2	$TeCl_4$ $TeCl_2$
S_2Br_2	$SeBr_4$ Se_2Br_2	$TeBr_4$ $TeBr_2$
	SeI_4 Se_2I_2	TeI_4 TeI_2
SO_2Cl_2 $SOCl_2$	$SeOCl_2$	$TeOCl_2$
HSO_3Cl	$H_2SeO_2Cl_2$	$H_2TeO_2Cl_2$
$S_2O_5Cl_2$	$SeOBr_2$	H_2TeCl_6

In general, the halogen compounds hydrolyze with water to form the hydrogen halide and the acid of the positive element. The latter may, however, be unstable in respect to decomposition into compounds of higher and lower valences.

The most important of these compounds is **sulfur monochloride,** S_2Cl_2. This is formed by the direct action of chlorine upon hot sulfur. It is a reddish yellow liquid and an excellent solvent for sulfur. For this reason, it is used in vulcanizing rubber. It is hydrolyzed by water: $2S_2Cl_2 + 2H_2O = SO_2 + 4HCl + 3S$. The other two chlorides may be formed by the action of chlorine upon cold monochloride, but are decomposed by gentle heating.

Sulfur dioxide reacts with chlorine, forming **sulfuryl chloride,** SO_2Cl_2. **Thionyl chloride,** $SOCl_2$, results from the reduction of phosphorus pentachloride by sulfur dioxide: $PCl_5 + SO_2 = SOCl_2 + POCl_3$. **Chlorosulfuric acid,** HSO_3Cl, is formed by the direct union of sulfur trioxide and hydrogen chloride. **Pyrosulfuryl chloride,** $S_2O_5Cl_2$, is formed by the direct union of sulfur trioxide and sulfuryl chloride.

32. Selenium and Tellurium with Sulfur.—There appear to be no compounds containing selenium and sulfur only, and the

two elements form several series of mixed crystals. The precipitate obtained by passing hydrogen sulfide into tellurous acid appears to be a mixture of the free elements and the sulfide TeS_2.

Concentrated sulfuric acid dissolves both selenium and tellurium with the formation of the compounds, $SeSO_3$ and $TeSO_3$, respectively, analogous to S_2O_3 (Par. 11).

Selenium may be substituted for sulfur in certain of the complex sulfur acids, e.g. seleno sulfuric acid, H_2SSeO_3.

33. Analytical.—Sulfur. The free element may be recognized by the pungent odor of sulfur dioxide upon burning; or by dissolving in hot alkali solution and placing a drop of the solution on a silver coin, a black stain, Ag_2S, indicating the presence of sulfur. Sulfides are detected by the liberation of hydrogen sulfide by dilute acids, which may be recognized by its odor, or by its reaction with moist lead acetate paper. Sulfates are detected by the precipitation of barium sulfate, which is not soluble in dilute acids. Since sulfur in the lower valences is readily oxidized to sulfate, this also constitutes a general method for the detection and estimation of sulfur. Thus in quantitative analysis, sulfur is usually precipitated and weighed as barium sulfate. Due to the occlusion of soluble salts by the barium sulfate, it is difficult to obtain the precipitate pure. This error is decreased by precipitating from a large volume, since the occlusion is proportional to the concentration of the soluble salts, and also by digesting the precipitate for some time, which allows the more soluble small crystals to dissolve and slowly recrystallize out on the larger crystals. If precipitated from cold concentrated solution, barium sulfate is so finely dispersed that it cannot be retained by ordinary filter paper.

Selenium. The free element dissolves in concentrated sulfuric acid to form a green solution, $SeSO_3$. In the ordinary scheme of analyses, selenates are precipitated by hydrogen sulfide as elementary selenium, which is soluble in ammonium polysulfide. Red selenium is precipitated from cool selenous acid solution by strong reducing agents, hydroxylamine hydrochloride, NH_2OH-HCl, being often employed. The precipitate turns black upon heating. A separation of selenium, arsenic, and germanium from the other elements may be made by distilling the material in solution with HBr and Br_2. The distillate consists of $SeBr_4$, H_3AsO_4, and $GeBr_4$.

In quantitative analysis, the selenium may be precipitated and weighed as the element, or determined volumetrically with oxidizing or reducing agents through the selenous-selenic acid couple.

Tellurium. Tellurium resembles selenium in its precipitation with hydrogen sulfide. The two elements may be separated by the hydrogen bromide treatment (cf. above) or by the reactions of the tetravalent acids with iodide in dilute acid, selenium precipitating as the red element, and tellurium forming a black precipitate, TeI_4, soluble in excess iodide to give a red solution of TeI_6^{--}. Tellurium may be weighed quantitatively as the metal or the dioxide. Tellurous acid may be oxidized by permanganate quantitatively to telluric acid.

CHAPTER XIII

CARBON

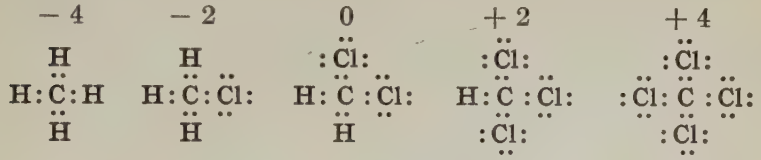
1. Several hundred thousand compounds of carbon are known, and the properties and reactions of these compounds constitute such a large portion of chemical knowledge that the whole of the science is now generally considered in respect to two great subdivisions, **organic chemistry** dealing with the carbon compounds, and **inorganic chemistry** dealing with the compounds of all the other elements.

It was once felt that the structure of the carbon compounds differed in some fundamental respect from that of the compounds of other elements, but it is now realized that their constitution can be correlated with the structure of the carbon atom and with the same general principles of compound formation which have been discussed in connection with the other periodic groups. This chapter will deal briefly with the structure of organic compounds in general and with the properties of the oxides and simpler carbon compounds. The relation of carbon to the other members of Group IV will be considered in the two subsequent chapters.

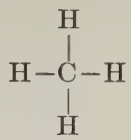
2. Structure of Carbon Compounds.—Carbon forms compounds in which the valence number varies from -4 to $+4$. However, the assignment of valence numbers in most of its compounds is so arbitrary as to be of little significance, that is, although we know the total number of valence electrons in the molecule, we are unable to say that a given number of electrons are definitely associated with a certain atom. The carbon atom, having four electrons, occupies a position intermediate to the elements which, on one side, lose their electrons to form positive ions, and on the other side add electrons to complete the octet and thus form negative ions. As a consequence of this position, it forms compounds in which it appears to complete the octet by sharing its electrons with other atoms. In terms of the idea that the pair of electrons constitutes a chemical bond, the behavior of carbon may be summarized by the statement: **carbon tends to form compounds in which it shares four pairs of**

electrons with the surrounding atoms. As an illustration of this statement and of the arbitrary nature of the polar valence number, the electron formulas of the simple carbon, hydrogen, chlorine compounds are given below (cf. also Hildebrand, *Princ. of Chem.*, p. 297).

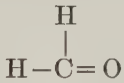
Valence Number:



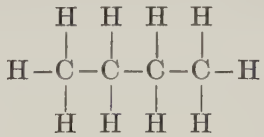
This idea of the four bonds of carbon has been of the greatest importance in the development of organic chemistry, and it is customary to represent these bonds by lines, e.g.



If one of the attached atoms is divalent, this is represented by drawing two bonds to it, e.g.



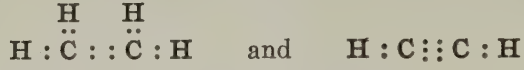
All of the carbon bonds are non-polar in nature; that is, dissociation into ions does not take place, due doubtless to the powerful field of force about the small carbon kernel with its charge of + 4. The most important consequence of the non-polar bonds is the formation of long chain carbon molecules, e.g.



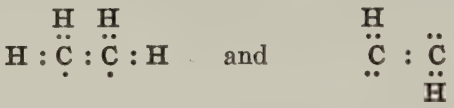
and of complicated compounds of very high molecular weight containing hundreds of atoms. Such compounds constitute plant and animal tissues; from which fact, the term organic chemistry has arisen.

Several types of compounds are formed in which the concept of the four bonds can only be kept by placing two or more of them between adjacent carbon atoms, e.g.

Such compounds are called "unsaturated." In terms of the "electron pairs" such compounds would be written as



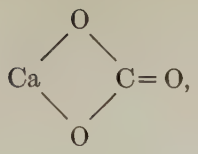
These formulas preserve the idea that carbon always has four bonds, but other electron arrangements appear to be at least equally probable, e.g.



It will be observed that the fundamental difference between saturated and unsaturated carbon compounds is that the latter lack sufficient electrons to complete all of the octets.

In general, the four valences are arranged in tetrahedral symmetry, the carbon atom being at the center and the four attached atoms at the corners of the tetrahedron (cf. Hildebrand, *Princ. of Chem.*, p. 297). In carbonates, however, such as calcium carbonate, $CaCO_3$, the solid is built up of a lattice of calcium and carbonate ions, and the carbonate ion has the three oxygen atoms arranged symmetrically about the carbon in the same plane:

This is a definite example of a compound in which the carbon does not possess four valence bonds, although its formula was formerly written as,



to indicate that such was the case (cf. also Hildebrand, *Princ. of Chem.*, p. 320).

3. Occurrence of Carbon.—Carbon occurs free in the crystalline forms of diamond and graphite. Coal is largely amorphous carbon, although it contains many complex compounds of carbon with hydrogen, as well as with oxygen and nitrogen. Methane, CH_4, is the principal constituent of natural gas; and heavier hydrocarbons constitute the mineral oils. The element is found most abundantly in the form of metal carbonates, limestone, or calcium carbonate, constituting one of the most common minerals. The occurrence of carbon in all animal and plant tissue has been mentioned.

4. Elementary Carbon.—Many of the physical properties of **diamond** and **graphite** may be correlated with their crystal structures. The diamond crystal is cubic and each carbon atom is surrounded by four other atoms located at the corners of a regular tetrahedron (Append. V). The four carbon valences are thus satisfied by carbon atoms, and the crystal is held together by bonds which are essentially the same as in the carbon compounds. As a result, diamond is the hardest known substance, and its melting point is probably higher than that of any other element. All of the electrons are doubtless held in the bonds between the atoms, and the crystal is, therefore, a non-conductor of electricity. Diamond has a very high index of refraction, 2.42; and this gives the cut gems a high brilliance, as most of the light falling upon them is totally reflected from the interior surfaces.

Graphite possesses hexagonal symmetry, and crystal structure data indicate planes of carbon atoms in hexagonal rings. Graphite is remarkably soft, and the crystal readily splits off thin flakes. The cleavage planes doubtless are identical with the planes of the carbon atoms of the crystal. Graphite is an electrical conductor, although only one thousandth as good as copper. This fact is in harmony with the crystal structure in that not all of the carbon bonds are satisfied, and some of the electrons are thus free to move through the crystal.

All forms of carbon are somewhat volatile at 3500°, and the vapor, upon condensing, forms graphite. Although the experimental data are somewhat uncertain, the most reliable heats of combustion lead to the value: $C_D = C_G + 180$ cal.; and it may be calculated from this value that diamond at one atmosphere pressure is unstable at all temperatures in respect to graphite. However, diamond is denser than graphite and under 8000 atmospheres at 25° it would become the stable form. Experimentally, it is possible to convert diamond into graphite by heating. Moissan prepared small diamonds by quenching solutions of carbon in molten metals. The contraction of the outer surface of the metal produces great pressure on the interior, thus favoring the formation of the diamond. Naturally occurring diamonds are thought to have been crystallized from solutions of molten magnesium silicates under conditions of great pressure.

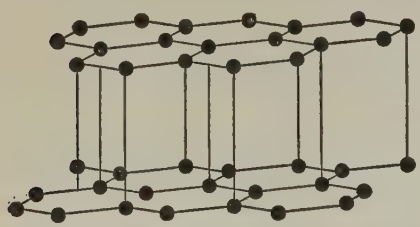


FIG. 1.—Crystal structure of graphite.

The so-called "**amorphous carbon,**" such as **charcoal,** appears upon examination by X-rays to resemble graphite in structure, except that it is highly porous or cellular. Upon oxidation by hot nitric acid and potassium chlorate, both charcoal and graphite yield **mellitic acid,** $C_6(CO_2H)_6$, a derivative of benzene, thus indicating the ring structure of the carbon in these substances (Par. 16). Charcoal possesses the property of absorbing gas, and, when cooled in liquid air, will absorb air from a sealed tube to produce a vacuum of 10^{-5} mm., or better. Highly active charcoal is used in gas masks for the absorption of poison vapors. The activation is carried out by heating for long periods in steam, which serves to remove adsorbed hydrocarbons from the surface. One cc. of active charcoal is said to have a surface of about 1,000 square meters. Bone charcoal is used in sugar refining to adsorb coloring matter present in the crude sugar.

Graphite has long been used for the manufacture of lead pencils. It is obtained from mines in Ceylon and Madagascar, and is now made in large quantities at Niagara Falls by heating anthracite coal in an electric furnace. Because of its infusibility,

it is used in making crucibles for use at high temperatures. The presence of a small portion of clay greatly increases its resistance to oxidation. Due to its high melting point, graphite is extensively used for electrodes in electric furnaces. Graphite, or gas carbon, is also used in arc lamp electrodes, cerium fluoride being often added to provide a metal vapor which increases the brilliance of the arc and also reduces its resistance. Ground in oil or water with tannin or other suspending agent, graphite forms a stable suspension, which is used in lubricating bearings. Graphite is also employed extensively in protecting metal surfaces from oxidation, e.g. in stove polish.

TABLE I

Atomic and Physical Properties of Carbon

Atomic weight	12	Ionization potential in volts, 1st electron		11.3
Atomic number	6	2d electron		24.3
Isotopes	None	3d electron		45.5
Electrons in various quantum levels, 1st	2	4th electron		64.2
2d	4	Melting point, °C	G	3500
Density	D 3.51	Boiling point, °C		4200
	G 2.25	Electrical resistivity, ohm-cm	D	5×10^{14}
			G	1.4×10^{-3}

Oxides and Acids

5. Carbon forms the monoxide, CO, which is the anhydride of carbonous or formic acid, HCO_2H, and the dioxide, CO_2, which is the anhydride of carbonic acid, H_2CO_3. In addition, several anhydrides of more complicated organic acids are known: e.g. carbon suboxide, C_3O_2, the anhydride of malonic acid, $CH_2(COOH)_2$.

Carbon monoxide is remarkably similar to nitrogen in physical properties (Table II). The two gases have the same molecular weight and also the same number (10) of valence electrons.

TABLE II

Properties of Carbon Monoxide and Nitrogen

	CO	N_2		CO	N_2
Melting point	−200°	−210°	Critical temperature	−140°	−146°
Boiling point	−190°	−196°	Critical pressure, atm.	36	35
Density of liquid	0.793	0.796	Critical volume, cc.	5.05	5.17

It seems probable from the similarity in properties that the arrangement of the electrons in both molecules is the same, possibly $\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathbf{N}}} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathbf{N}}}$ and $\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathbf{C}}} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathbf{O}}}$.

Carbon monoxide is but slightly soluble in water, 3 cc. per 100 cc. of water at 8°. It is more soluble in alkalies, giving formates: $CO + NaOH = HCOONa$. The gas is readily prepared in the laboratory by the action of sulfuric acid on formic or oxalic acid, or ferrocyanide: (1) $HCOOH = CO + H_2O$, (2) $H_2C_2O_4 = CO + CO_2 + H_2O$, (3) $K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = 6CO + 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4$. The formation from reactions involving carbon, oxygen, and water is discussed in later paragraphs.

Carbon monoxide reacts with many metals, forming **carbonyls,** e.g. $Fe(CO)_5$, $K_6(CO)_6$, $Ni(CO)_4$, $Co(CO)_4$, $Mo(CO)_6$. The nickel compound is of especial importance (cf. **XIX—20**). The potassium carbonyl appears to be a derivative of benzene, $C_6(OK)_6$. The oxide enters into a number of "coordination complex ions" such as $K_3Fe(CN)_5CO$; and the gas is absorbed by both acid and ammonical solutions of cuprous chloride with the formation of rather unstable complexes, possibly $Cu(CO)Cl_2^-$, and $Cu(CO)NH_3^+$. Such solutions are employed in gas analysis in the estimation of carbon monoxide, although small amounts of the gas are more accurately determined by passing the gas over hot (160°) iodine pentoxide: $5CO + I_2O_5 = 5CO_2 + I_2$. The iodine is absorbed in iodide solution and titrated with thiosulfate.

Carbon monoxide unites directly with chlorine in the sunlight, or in the presence of active charcoal as a catalyst to form **phosgene, carbonyl chloride,** $COCl_2$. The reaction is highly exothermic, and is, therefore, favored by low temperatures (below 350°).

Carbon monoxide is extremely poisonous. Air containing 1 part in 500 will cause unconsciousness in about an hour; and 1 part in 100 will cause death in a few minutes. The physiological action is due to the formation of a bright red compound with the haemoglobin of the blood. Gas masks to protect against carbon monoxide contain a mixture of manganese and copper oxides known as "hopcalite," which acts as a catalyst for the oxidation of the gas to carbon dioxide.

6. **Equilibria Involving Carbon Monoxide and Dioxide.**—Around 500° C., carbon (in excess), in an atmosphere of oxygen,

gives almost completely carbon dioxide: $C + O_2 = CO_2$ (1), but at 1000°, the reaction (with excess carbon) gives almost pure carbon monoxide: $2C + O_2 = 2CO$ (2). It follows that in the equilibrium: $C + CO_2 = 2CO$ (3), high temperature favors the formation of the lower oxide. Data on the equilibrium are given in Table III.

TABLE III

$C(graph) + CO_2 = 2CO$

$t°$ C.	500	600	800	1000	1200
Per cent CO_2	95	77	7	0.6	0.06

At low temperatures, carbon monoxide is unstable with respect to the decomposition (3) above, but the rate of decomposition is extremely slow; however, around 300° platinum or nickel act as efficient catalysts.

Wish excess oxygen, both carbon and carbon monoxide are oxidized to the dioxide: $2CO + O_2 = 2CO_2$ (4). Only at extremely high temperatures is reaction (4) reversed and carbon dioxide dissociated (Table IV). The union of carbon monoxide and oxygen is slow at low temperatures, and even at high temperatures, if the gases are perfectly dry. Water, therefore, appears to act as a catalyst.

TABLE IV

$CO_2 = CO + \frac{1}{2}O_2$

$t°$ C.	1122	1550	2000	2600
Per cent CO_2 dissociated	0.01	0.4	2	50

The equilibrium: $C + H_2O(g) = CO + H_2$ (5) is very important in the manufacture of artificial fuel gas (see below). At 25°, the equilibrium constant is about 10^{-16}, but at 600° it is about 1; hence there is a rapid change in the direction of the reaction with temperature.

Below 500°, steam will oxidize carbon monoxide: $CO + H_2O_{(g)} = CO_2 + H_2$ (6). This reaction is utilized in the preparation

of commercial hydrogen from water gas (Par. 7). Data on the equilibrium are given in Table V.

TABLE V

$CO + H_2O_{(g)} = CO_2 + H_2$

$t°$ C.....	400	500	600	800	1000
Per cent CO converted...	94	86	76	53	38

Reactions between carbon monoxide and hydrogen to form hydrocarbons and alcohols are discussed in Paragraph **33.**

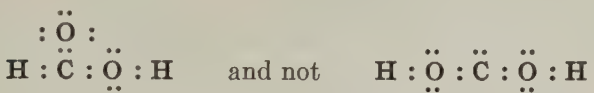
The frequent mention of carbon monoxide in metallurgical processes arises through its powerful reducing power, which enables it to remove oxygen from metal oxides: e.g. $CuO + CO = CO_2 + Cu$ (7). The more noble the metal, the greater the tendency for reaction (7) to take place. In certain cases, the reaction is complicated by the formation of carbides.

7. Carbon Monoxide Fuels.—Carbon monoxide is an important constituent of several artificial fuels. When a limited supply of air is passed through coke or anthracite coal, the resulting mixture is known as **producer gas,** and contains carbon monoxide (30 to 40 per cent), nitrogen (60 per cent), and hydrogen (2 to 5 per cent). A gas of somewhat similar composition, called **blast furnace gas,** is a product of iron smelting. The most important artificial gas, however, is **water gas,** made by passing steam over hot coal. The reaction is endothermic (see reaction (5) above) and in order to maintain the required temperature (around 600°), it is necessary to turn off the steam every few minutes and blow air in for a brief period. The resultant mixture of gases consists of carbon monoxide (40 to 50 per cent), hydrogen (45 to 50 per cent), carbon dioxide (3 to 7 per cent), and nitrogen (4 to 5 per cent). In certain localities where crude oil is cheap and coal expensive, **oil-water gas,** for cooking and heating, is made by spraying crude oil and steam upon heated bricks. The heavy hydrocarbons are "cracked" by the heat into carbon and lighter gases, such as CH_4 and C_2H_6; the former reacts with the steam to form carbon monoxide and hydrogen.

8. Formic or Carbonous Acid.—Carbon monoxide reacts with alkalies producing formates, but does not react with water

at ordinary temperatures. However, the equilibrium: $CO + H_2O = H(HCO_2)$ is attainable at 150° in the presence of hydrogen chloride with the system under pressure; and from measurements of this equilibrium, it may be calculated that formic acid is stable at room temperature with respect to carbon monoxide at one atmosphere. Sulfuric acid readily removes the water from formic acid and evolves carbon monoxide.

Formic acid appears to have the formula



and not

In this respect, it is similar to the lower valent acids of phosphorus, and like them it is a stronger acid than the higher valent acid. The acid is monobasic, and the dissociation constant is 2.4×10^{-4}. The acid has a pungent, irritating odor, and blisters the skin like a nettle sting. All of the formates are soluble, but the silver and lead salts only moderately.

9. Carbon Dioxide.—The product of the oxidation of carbon, free or combined, with excess of oxygen is the dioxide, CO_2. This oxide is also formed by the action of acids upon carbonates: $CaCO_3 + H_2SO_4 = CaSO_4 + H_2O + CO_2$; or by the thermal decomposition of carbonates or bicarbonates: $MgCO_3 = MgO + CO_2$. An important commercial source of the oxide is the alcoholic fermentation of sugars: $C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$.

Carbon dioxide occurs in the atmosphere in amounts varying from 3 parts in 10,000 in the country, to 1 part in 100 in crowded and poorly ventilated rooms. It also occurs in effervescent mineral waters, and issues from the ground in large quantities in certain localities, as the Valley of Death, in Java.

Solid carbon dioxide has a vapor pressure of 1 atmosphere at − 78.5°, and therefore sublimes at that temperature. If heated under pressure, it melts at − 56° (5.3 atm.). The critical temperature of the liquid is 31.35°, the critical pressure, 73 atmospheres. The vapor pressure at 20° is 59 atmospheres. The oxide is usually handled commercially as the liquid in steel cylinders. If the liquid is allowed to flow from the cylinder into a heavy cloth bag, the heat of vaporization is sufficient to cool a large fraction of the oxide to the solid state, forming carbon dioxide snow. A solution of the solid in acetone under

reduced pressure may be employed to obtain temperatures around − 110°.

The solubility of carbon dioxide in water at 1 atm. pressure and various temperatures is:

$t°$ C	0	25	40	60
g. CO_2 per 100 g. H_2O	0.355	0.145	0.097	0.058

Up to about 5 atmospheres, the solubility is nearly proportional to the pressure, following Henry's law, but above that pressure the solubility becomes greater due to the formation of carbonic acid. Soda water contains carbon dioxide under a pressure of 3 to 4 atmospheres.

Carbon dioxide is not poisonous; its harmful effects are due rather to suffocation through lack of oxygen. Air containing 2 to 3 per cent of the gas may be breathed without apparent ill effect, but above 5 per cent panting is produced; and 50 per cent carbon dioxide can be tolerated only for a short time. The high humidity of badly ventilated rooms is probably more harmful than the carbon dioxide content.

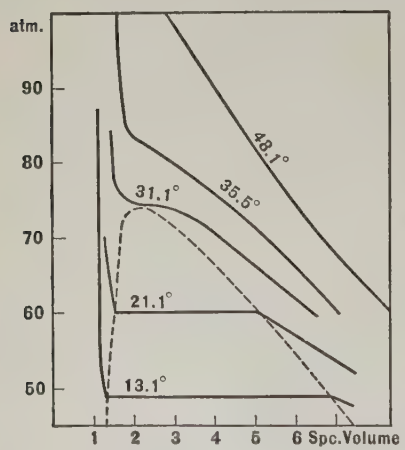


Fig. 2.—Pressure-volume curves for CO_2.

The principal use of carbon dioxide is in the preparation of carbonated beverages. Liquid carbon dioxide is used in refrigeration cycles; the solid is used in cold storage, in place of ice, especially in shipping fruit, as the gas liberated tends to prevent the development of aerobic bacteria. The gas is employed in the manufacture of certain carbonates, including the sodium carbonates and white lead. Carbon dioxide is generated in the soda-sulfuric acid type of fire extinguisher. A few per cent of carbon dioxide in air will render it a non-supporter of combustion.

Carbon dioxide is absorbed from the atmosphere by plants, and is the source of the cellulose in plant tissue: $6CO_2 + 5H_2O = C_6H_{10}O_5 + 6O_2$. This reaction (or related reactions) requires the absorption of energy; this is supplied by sunlight through the agency of the chlorophyll. It is this absorption of radiation by plants, that renders the sun's energy available to us through the use of plants as food, and of plant products, wood, coal, etc., as fuel. The decomposition of plant tissue, of course, returns carbon dioxide to the atmosphere, and this continuous absorption and evolution of carbon dioxide by plants is sometimes referred to as the **carbon cycle.**

10. Carbonic Acid.—The structure of carbonic acid has been discussed (Par. 2). The acid is known only in solution, in which it doubtless exists as the meta- rather than the ortho-form. At 1 atmosphere of CO_2 and 25° C., a water solution contains $0.0338M$ H_2CO_3. The acid is weak, the dissociation constants being, respectively: $K_1 = 3.5 \times 10^{-7}$, and $K_2 = 3.7 \times 10^{-11}$. A saturated solution (1 atm.) thus contains $10^{-4}M$ H^+.

Due to the weakness of carbonic acid, solutions of the normal carbonates are alkaline from hydrolysis: $CO_3^{--} + H_2O = HCO_3^- + OH^-$. The concentration of OH^- in $0.5M$ Na_2CO_3 is about $0.01M$. Bicarbonate ion can either hydrolyze,

$$HCO_3^- + H_2O = H_2CO_3 + OH^-,$$

or it can ionize further,

$$HCO_3^- = CO_3^{--} + H^+.$$

The former reaction proceeds farther than the latter, as is shown by the faintly alkaline character of bicarbonate solutions; the concentration of OH^- in a molal solution is 10^{-6}. However, the two reactions tend to assist each other, due to the neutralization of H^+ and OH^-; each goes farther than it would in the absence of the other, giving as the result the summation in the reaction,

$$2HCO_3^- = H_2CO_3 + CO_3^{--}.$$

The equilibrium constant for this very important reaction is 1.06×10^{-4}, corresponding to about $0.01M$ CO_3^{--} and $0.01M$ H_2CO_3 in M $NaHCO_3$. Because of this equilibrium, carbonates are readily converted to bicarbonate by passing carbon dioxide into their solutions; or, if they are but slightly soluble, into a

suspension in water. The most important example of such a conversion is the solution of calcium carbonate in excess carbon dioxide: $CaCO_3 + H_2CO_3 = Ca^{++} + 2HCO_3^-$. The equilibrium is displaced upon heating by the evolution of carbon dioxide, hence bicarbonates in solution form carbonates upon heating, upon evaporation, or upon neutralization of the carbonic acid. The first of these processes accounts for the formation of scale in kettles and boilers; the second for the formation of stalactites and stalagmites in caves; and the third is used in the softening of water by addition of alkaline reagents, such as ammonia, or by the exactly equivalent amount of calcium hydroxide (cf. V—11).

With the exception of the alkali metals, most of the carbonates are but slightly soluble or else hydrolyze to form basic carbonates or hydroxides. The bicarbonates of the alkali metals are less soluble than the carbonates; those of other metals generally more soluble. Reference should be made to the alkali carbonates for the details of their commercial preparation.

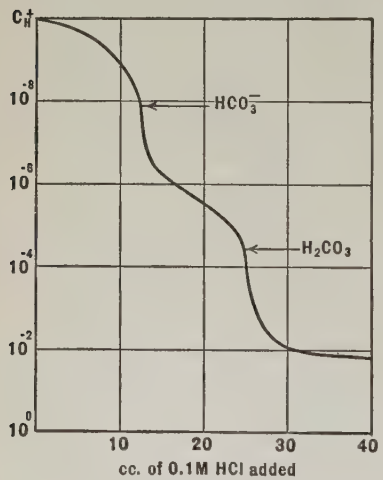


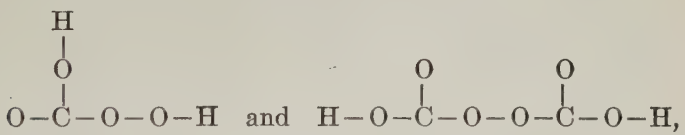
FIG. 3.—Titration of carbonate with hydrochloric acid.

11. Analysis of Carbonates.—Carbonates are detected in qualitative analysis by the evolution of carbon dioxide with acids, and the formation of a white precipitate when this is passed into a solution of barium or calcium hydroxide. When only a trace of carbonate is present, the test is made more delicate by adding a small piece of zinc to the sample, so that the hydrogen evolved will carry the carbon dioxide through the lime water.

The indicator, methyl orange, changes from yellow to red at about $10^{-4}M$ H^+; hence, a dilute solution of carbonic acid gives a yellow color; but if a drop of strong acid is added, the color changes to red. Carbonates may, therefore, be titrated with a strong acid, using this indicator. An alternate method is to add

an excess of standard acid, remove the carbonic acid by boiling, and titrate the excess of acid with alkali, using phenolphthalein as an indicator. In case hydroxide is present, the carbonate may first be removed by precipitation as barium carbonate. In a mixture of soluble carbonate and bicarbonate, the solution may first be titrated with a strong acid, using phenolphthalein as an indicator, which gives the amount of carbonate. Methyl orange is then added, and the titration is continued with acid. The second step corresponds to the sum of the carbonate and bicarbonate. Or, the analysis may be made (1) by addition of excess of standard base, (2) precipitation of the carbonate by barium ion, (3) filtration of the carbonate and determination of total carbonate by titration, (4) titration of hydroxide in the filtrate to give amount of carbonate by difference.

12. Peroxycarbonates.—Salts of the type K_2CO_4 and $K_2C_2O_6$ are known, corresponding to the acids



but the free acids are unstable. The monoperoxycarbonates are formed by the interaction of an alkali carbonate and hydrogen peroxide. They may be precipitated from the solution by ether. The salts of the diperoxycarbonic acid may be prepared by the anodic oxidation of solutions of alkali carbonates, cooled to $-10°$ or below. These compounds show the characteristic strong oxidizing power and strong reducing power of other peroxyacids and of hydrogen peroxide.

13. Carbides.—Carbon combines directly with many metals at high temperatures to yield carbides. All the main Group I metals form carbides of the general formula, M_2C_2; and the main Group II (except beryllium), MC_2. These compounds hydrolyze in water with the evolution of acetylene. The rare earth metals form carbides of the same general formula, MC_2, but these and other dicarbides, as ZrC_2, ThC_2, and MnC_2, hydrolyze to form complex mixtures of solid and liquid hydrocarbons. Beryllium carbide, Be_2C, aluminum carbide, Al_4C_3, and a number of group four compounds, as SiC, TiC, and ZrC, hydrolyze to form methane. In addition, there exists a number of

comparatively nonreacting carbides as B_6C, Fe_3C, Mn_3C, Cr_4C, Cr_3C_2, W_2C, VC, Mo_2C, and MoC. No carbides are formed by members of the first or the second subgroups, or by tin, lead, arsenic, antimony, or bismuth.

Commercially, the most important carbide is **calcium carbide.** This is made by heating a mixture of lime and carbon in an electric furnace (about 3000°): $CaO + 3C = CaC_2 + CO$. The reaction is highly endothermic. The formation of acetylene and cyaniamide from the carbide is discussed under those compounds.

14. Carbon and Sulfur.—The **disulfide,** CS_2, is formed from sulfur vapor and graphite at very high temperatures, but the equilibrium is reversed at low temperatures. It is, therefore, prepared by heating carbon and sulfur in an electric furnace: $C + 2S = CS_2$.

The compound is a heavy, colorless, volatile, highly refractive liquid. It usually has a disagreeable odor from the presence of other sulfur compounds. It has acid properties, and unites with basic sulfides forming thiocarbonate: $BaS + CS_2 = BaCS_3$. The liquid is a good solvent. The vapor is highly inflammable and poisonous. It is used in killing rodents, as a solvent for rubber and sulfur, and in the preparation of carbon tetrachloride.

The **monosulfide,** CS, is prepared by the action of ozone upon carbon disulfide vapor. It may be condensed as a liquid at very low temperatures; upon heating, it polymerizes with explosive violence to a solid.

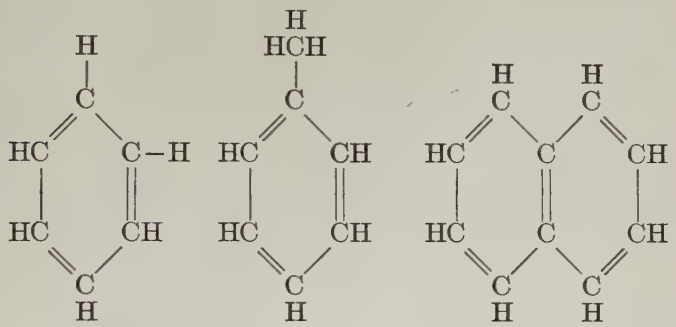
15. Carbon oxysulfide, COS, forms when carbon disulfide is treated with sulfur trioxide: $CS_2 + 3SO_3 = COS + 4SO_2$. It is a colorless gas, and resembles carbon dioxide in being rather soluble in water.

16. Carbon and Hydrogen.—The formation of heavy hydrocarbon molecules has been discussed in the introductory paragraphs of this chapter. These compounds may be considered in two main groups.

(1) The **aliphatic** compounds. The paraffin series, general formula, $C_nH_{(2n+2)}$, occurs extensively in American mineral oils. The lighter members of the series, CH_4 to C_4H_{10}, constitute natural gas. The compounds, C_5H_{12} to C_8H_{18}, constitute the light and heavy gasolines. The members, C_9H_{20} to $C_{13}H_{28}$, are familiar as lubricating oils, and heavier molecules, up to $C_{35}H_{72}$, as paraffin wax. Various unsaturated derivatives of the paraffins

(Par. 2) may be considered as separate series: such as compounds of the general type, C_nH_{2n}, the olefine series, and C_nH_{2n-2}, acetylene series.

(2) **Aromatic** compounds, consisting of benzene, C_6H_6, and its simple derivatives, such as toluene, $CH_3C_6H_5$; and more complicated double and triple ring compounds, such as naphthalene, $C_{10}H_8$, and anthracene, $C_{14}H_{10}$.



These hydrocarbons occur in certain types of mineral oils, and in the liquid, condensate from the destructive distillation of coal.

17. Methane, CH_4, has been mentioned as the principal constituent of natural gas. It was formerly known as marsh gas, and was first observed as bubbles rising from the decomposition of vegetable matter in swamps. The gas has a low freezing and boiling point, and is but slightly soluble in water (5.5 cc. per 100 cc. of water at 0°).

The gas may be formed by the direct reaction of carbon and hydrogen, at moderately high temperatures, Table VI.

TABLE VI

EQUILIBRIUM VALUES FOR THE REACTION,

$C + 2H_2 = CH_4 + 183{,}000$ cal.

$t°$ C	400	600	800	1000	1200
Per cent CH_4	86	32	4	1	0.2

The reaction is obviously favored by high pressure.

Methane is also formed by the reaction of carbon monoxide and hydrogen: $CO + 3H_2 = CH_4 + H_2O$, at low temperatures, 250°–300°, in the presence of certain catalysts (Par. **33**). At high temperatures, the equilibrium is reversed.

The laboratory preparation of methane is usually carried out by heating a mixture of sodium acetate and soda lime, or by the action of water on aluminum carbide: $CH_3COONa + NaOH = Na_2CO_3 + CH_4$, and $Al_4C_3 + 12H_2O = 3CH_4 + 4Al(OH)_3$.

18. Acetylene, C_2H_2, is formed in small amounts by the reaction of carbon and hydrogen at very high temperatures (2500°): $2C + H_2 = C_2H_2$. It is prepared commercially by the action of water on calcium carbide: $CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2$.

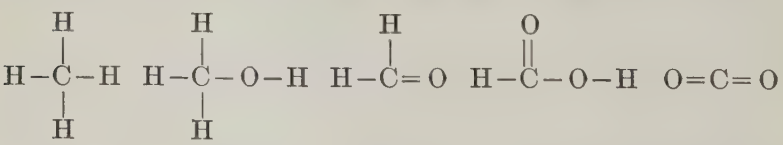
The gas is colorless and odorless when pure, but usually has a pungent odor due to the presence of traces of phosphine. The vapor pressure of the liquid is about 40 atmospheres at 20°; and under these conditions it is highly explosive, as at ordinary temperatures the gas is unstable in respect to hydrogen and carbon. It is usually handled as a solution in acetone under pressure in steel cylinders.

The temperature of the oxy-acetylene torch, 2500 to 3000° C., is hotter than that of any other flame, with the possible exception of that of atomic hydrogen (cf. **I—9**); and this is employed extensively in cutting and welding steel and other metals. Before the introduction of the incandescent electric globe, the acetylene lamp was of considerable importance.

Acetylene acts as a very weak acid. Silver acetylide, Ag_2C_2, is formed by passing the gas through a solution of silver ammonia hydroxide. Many of the acetylides are explosive.

As an unsaturated compound, it readily adds hydrogen or halogens to form, respectively, ethane or its halogen derivatives of the type $C_2H_2X_4$.

19. Oxidation Products of the Hydrocarbons.—The oxidation of methane leads to the following series of oxidation products:



Methane	Methyl alcohol	Formalde-hyde	Formic acid	Carbon dioxide.

The number of electrons involved in the various oxidations is indicated by the following half reactions:

$$CH_4 + H_2O = CH_3OH + 2H^+ + 2E^-$$
$$CH_3OH = HCHO + 2H^+ + 2E^-$$
$$HCHO + H_2O = HCOOH + 2H^+ + 2E^-$$
$$HCOOH = CO_2 + 2H^+ + 2E^-$$

Related compounds result from the oxidation of other hydrocarbons; and these compounds are generally classified on the basis of the following characteristic groups, where R represents an organic radical formed by the removal of one hydrogen ion from a hydrocarbon, e.g. ethyl, C_2H_5, from ethane, C_2H_6.

$R-OH$ Alcohols—organic bases

$$R-C(=O)-H$$ Aldehydes

$$R-C(=O)-R$$ Ketones

$$R-C(=O)-OH$$ Acids

$$R-O-R$$ Ethers—by removing water from two alcohol molecules

$$R-C(=O)-OR$$ Esters—" salts " of an alcohol and organic acid.

20. Carbohydrates.—An important class of organic compounds contain hydrogen and oxygen in the same proportion as in water, and are termed carbohydrates. The group includes **cellulose,** $(C_6H_{10}O_5)_y$, starch, $(C_6H_{10}O_5)_x$, and the sugars. The latter are generally classified as **monosaccharides,** $C_6H_{12}O_6$, such as **glucose** or **fructose**; and as **disaccharides,** $C_{12}H_{22}O_{11}$, such as **sucrose** (cane sugar), or **lactose** (milk sugar). These compounds are really alcohol, and aldehyde or ketone derivatives of long

chain hydrocarbons, e.g. glucose is $CH_2OH \cdot CHOH \cdot CHOH \cdot CHOH \cdot CHOH \cdot CHO$.

The molecular weights of cellulose and starch are not known, but the molecules are very complex. Starch may be converted to glucose by boiling in a solution containing a little hydrochloric acid: $(C_6H_{10}O_5)_x + xH_2O = xC_6H_{12}O_6$. Under similar conditions, sucrose may be hydrolyzed to a mixture of glucose and fructose.

21. Halogens and Hydrocarbons.—Any hydrogen in a hydrocarbon is capable of being replaced by a halogen atom, thus making possible thousands of halogen hydrocarbon derivatives. The replacement can often be accomplished by direct action of the halogen as a gas, or in alkaline solution upon the hydrocarbon, e.g. $C_2H_6 + Cl_2 = C_2H_5Cl + HCl$. Reactions between alcohols and halogen acids may also be employed: $C_2H_5OH + HCl = C_2H_5Cl + H_2O$. A few of the more important compounds are discussed below.

Carbon tetrachloride, CCl_4, is made by passing a mixture of carbon disulfide vapor and chlorine through a red hot tube: $CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2$. The tetrachloride may be separated by fractional distillation from the sulfur chloride. Or, the reaction may be carried out by passing chlorine gas through the disulfide in the presence of a small amount of iodine. Carbon tetrachloride is a heavy, colorless liquid. It is non-inflammable, and a good solvent for non-polar substances; whence its use in dry cleaning, and in fire extinguishers, e.g. "pyrene." The vapors are slightly toxic.

Chloroform, $CHCl_3$, is prepared by the action of bleaching powder on alcohol. It is a heavy liquid, and is used largely as an anaesthetic.

Iodoform, CHI_3, is prepared by the action of iodine in alkaline solution on alcohol. It is a solid with a pungent characteristic odor, and finds extensive use as an antiseptic.

Ethyl Chloride, C_2H_5Cl, is formed when ethane is treated with chlorine in the sunlight, or alcohol is treated with phosphorus pentachloride. It is a volatile liquid which is employed in refrigerant cycles, and as a local anaesthetic.

22. Carbon and Nitrogen.—The nitride, C_2N_2, **cyanogen,** may be considered as the polymerized free cyanide radical, since it is formed by the oxidation of cyanides. The chemistry of

the cyanides resembles in many respects that of the halogens, especially iodine; and the methods of preparation of cyanogen, by heating the compounds of the noble metals, and by the reaction with cupric ion, are analogous to the liberation of iodine under these conditions: $2AuCN = 2Au + C_2N_2$, $Hg(CN)_2 = Hg + C_2N_2$, $2Cu^{++} + 4CN^- = 2CuCN + C_2N_2$. The reaction, $C_2N_2 = 2C + N_2$, is highly exothermic (about 80,000 cal.). Many references are made in the chemical literature to the formation of cyanogen in the electric arc, but it is doubtful if, even at that high temperature, an appreciable quantity of the compound can be formed by direct union of the elements.

Cyanogen is a colorless gas, has a distinctive odor, and is extremely poisonous. It is soluble in water (4 volumes per 1 volume of water at 0°). When heated to 400° the gas polymerizes to a white solid, **paracyanogen,** $(CN)_x$. In alkaline solution, cyanogen hydrolyses to cyanide and cyanate: $C_2N_2 + 2OH^- = CN^- + CNO^- + H_2O$ (compare $Cl_2 + 2OH^- = Cl^- + ClO^- + H_2O$). In sunlight, it decomposes, forming ammonium oxalate, ammonium formate, and urea.

23. Hydrogen Cyanide, or " prussic acid," may be prepared by the action of dilute sulfuric acid upon an alkaline cyanide, as it is a weak volatile acid. With concentrated sulfuric acid, carbon monoxide is evolved: $HCN + H_2O + H^+ = CO + NH^+_4$. The acid is also liberated by the dehydrating action of phosphorus pentoxide upon ammonium formate: $HCOONH_4 = HCN + 2H_2O$. Compounds of hydrogen cyanide with sugars (glucosides) occur in nature, e.g. in leaves and seeds of the peach tree; a solution made by boiling peach leaves in water was used by the ancient Egyptians as a poison.

Liquid hydrogen cyanide boils at 26.5°. The gas has the odor of bitter almonds, and is extremely poisonous. It is readily soluble in water, like the halogen acids; but unlike them it is a weak acid, $K_{18°} = 1.32 \times 10^{-9}$. With chlorine in solution **cyanogen chloride** is formed: $HCN + Cl_2 = HCl + CNCl$. Alkaline oxidizing agents oxidize cyanide to cyanate (see below), while acid oxidizing agents usually yield carbon dioxide and ammonia.

The arrangement of the 10 electrons in cyanide ion is unknown (: C : : $\ddot{\text{N}}$: or : C : : N : or $\ddot{\text{C}}$: $\ddot{\text{N}}$:?). When the bond between the carbon and nitrogen is broken by hydrolysis, however, 8 of

the 10 electrons go with the nitrogen forming ammonium: thus, $HCN + 2H_2O = HCOONH_4$ (ammonium formate), and $C_2N_2 + 4H_2O = \begin{vmatrix} COONH_4, \\ COONH_4 \end{vmatrix}$ ammonium oxalate.

24. The Alkali Cyanides are important commercial compounds (cf. **IV—21**). They may be prepared: (1) from alkali ferrocyanide by fusion with sodium metal: $K_4Fe(CN)_6 + 2Na = 4KCN + 2NaCN + Fe$; (2) by heating the ferrocyanide with carbonate: $K_4Fe(CN)_6 + K_2CO_3 = 5KCN + KCNO + CO_2 + Fe$; (3) by the reactions: $2NH_3 + 2Na = 2NH_2Na + H_2$ (300°–400° C.) and $2NaNH_2 + 2C = 2H_2 + 2NaCN$ (red heat; (4) from calcium cyanamide by fusion with sodium carbonate: $CaCN_2 + C + Na_2CO_3 = CaCO_3 + 2NaCN$; (5) by the Bucher process for the fixation of nitrogen, by heating a mixture of sodium carbonate, carbon, and iron (catalyst) made into bricks in an atmosphere of nitrogen: $Na_2CO_3 + 4C + N_2 = 2NaCN + 3CO$. The cyanide is extracted with liquid ammonia.

The alkali cyanides are readily soluble in water, and the solutions are somewhat alkaline by hydrolysis. Reference should be made to iron, silver, and gold for the important complex cyanides of those elements. Complex ions of the type, $M(CN)_4^{--}$, are formed by Zn^{++}, Pt^{++}, Ni^{++}, Cd^{++}; of the type, $M(CN)_6^{---}$, by Co^{+++}, Mn^{+++}, Fe^{+++}, Cr^{+++}; and of the type, $M(CN)_6^{----}$, by Co^{++}, Fe^{++}, Mn^{++} and Cr^{++}.

25. Cyanates are readily prepared by the action of mild oxidizing agents upon cyanides, for example, by heating potassium cyanide with lead oxide: $KCN + PbO = KCNO + Pb$. The salt is extracted from the lead with alcohol, as the water solution is unstable: $KCNO + 2H_2O = NH_3 + KHCO_3$. Cyanate is also formed by the action of cyanide upon copper ammonia ion: $2Cu(NH_3)_4^{++} + 3CN^- + 2OH^- = 2CuCN + CNO^- + 8NH_3 + H_2O$. The cyanide-cyanate potential

$$CN^- + 2OH^- = CNO^- + H_2O + 2E^-; \text{ is } + 0.97 \text{ volts.}$$

The free acid decomposes very readily into carbon dioxide and ammonia in water solution. **Ammonium cyanate,** NH_4CNO, is isomeric with **urea:** $NH_4CNO = CO(NH_2)_2$. The rearrangement takes place upon evaporating an aqueous solution.

26. Thiocyanates may be prepared by fusing alkali cyanides with sulfur: $KCN + S = KCNS$. The ammonium salt is formed by the reaction of ammonia and carbon disulfide: $4NH_3 + CS_2 = NH_4CNS + (NH_4)_2S$. At 140°, this salt rearranges to **thiourea,** $CS(NH_2)_2$. The free acid, HCNS, is a liquid which readily polymerizes to a yellow solid.

27. Calcium Cyanide is important in its relation to the cyanamide process for the fixation of nitrogen. Around 1000°, calcium carbide absorbs nitrogen to form cyanamide: $CaC_2 + N_2 = CaCN_2 + C$. The product is used directly as a fertilizer, or treated with superheated steam to convert the nitrogen into ammonia: $CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$. At low temperatures, the hydrolysis product is cyanogenamide: $2CaCN_2 + 4H_2O = 2Ca(OH)_2 + (CNNH_2)_2$. The world's production of cyanamide in 1926 was about 500,000 tons. It is probable that the production will decrease, due to the cheaper direct synthesis of ammonia from its elements. The preparation of cyanide from cyanamide has been mentioned above.

28. The proteins constitute a class of extremely complicated nitrogen compounds, occurring in animal and vegetable tissue. Empirical formulas, calculated from the percentage composition, give results such as $C_{146}H_{226}N_{44}SO_{50}$, but the molecular weights appear to be much higher. The proteins are complexes of amino-acids, i.e. compounds containing the groups $NH_2\overset{|}{\underset{|}{C}}-$ and $-COOH$, such as glycine, CH_2NH_2COOH.

The Organic Chemical Industries

Many references have been made to the use of inorganic chemicals in various organic industries. For the sake of clarifying these references, brief outlines of some of the more important industries will be given.

29. Explosives.—One of the most important explosives is **nitroglycerine** (cf. also **XII—36**). This compound is very easily detonated by shock: $4C_3H_5(NO_3)_3 = 12CO_2 + 10H_2O + 6N_2 + O_2$. Like all good explosives, the heat of the reaction is large, and the gaseous products tend to occupy a very large volume in comparison to the original compound. **Dynamite** was formerly made by absorbing nitroglycerine in a porous earth;

this form is now generally replaced by solutions of guncotton in nitroglycerine, known as **blasting gelatine,** giant powder, etc. Diethylglycol dinitrate, $C_2H_4(NO_3)_2$, is now being used somewhat in place of nitroglycerine. **Guncotton,** or cellulose trinitrate, $C_6H_7O_2(NO_3)_3$, is formed by steeping cotton in a cold mixture of nitric and sulfuric acids. It explodes when detonated by another explosive. **Smokeless powder,** or **cordite,** is made by evaporating a solution, in acetone, of guncotton, nitroglycerine, and a little vaseline.

The high explosives employed in shells to produce violent shattering are **trinitrotoluene,** "TNT," $CH_3C_6H_2(NO_2)_3$, and **picric acid,** $C_6H_2(OH)(NO_2)_3$. A mixture of the former with ammonium nitrate is known as **amatol.**

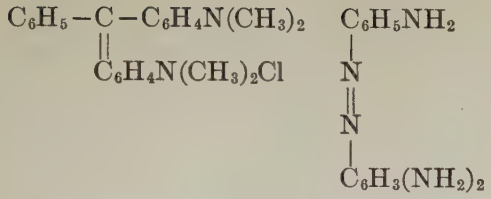
30. Plastics.—Wood pulp, cotton, or other cellulose, dissolve in sodium hydroxide and carbon disulfide to form a solution known as **viscose:** $C_6H_{10}O_5 + NaOH + CS_2 = C_6H_9O_5CS_2Na + H_2O$. When this is coagulated in a bath of sulfuric acid, a very plastic form of cellulose is obtained. This may be rolled into transparent films for wrappers for candy, etc.; or pressed through dies into solutions of ammonium salts to give **"rayon,"** or other artificial textiles. Approximately 200 million pounds of viscose are now produced yearly.

Cotton treated with acetic anhydride, $(CH_3CO)_2O$, forms **cellulose acetate.** This dries to a very tough transparent film, and is used in making picture-films, artificial horse hair, etc.

A number of nitrocellulose compounds form plastics when dissolved in suitable solvents. Among these are **celluloid, collodion,** and various forms of artificial leather.

Another type of plastics is the artificial ambers, as, for example, **Bakelite,** formed by the condensation of phenol, C_6H_5OH, with formaldehyde, CH_2O, or with other aldehydes, as furfural, $C_5H_4O_2$.

31. Dyes, Perfumes, and Drugs.—Compounds of aromatic hydrocarbons constitute almost 100 per cent of textile dyes. Many of these compounds are synthesized from aniline, $C_6H_5NH_2$, obtained from the distillation of coal tar. Examples of important types of color compounds are given below:



Malachite green Bismark brown Phenolphthalein

The flavors and perfumes are largely esters and aldehydes, such as "banana oil," amylacetate, $CH_3COOC_5H_{11}$. The organic drugs embrace a large number of different types of compounds. The **alkaloids,** as morphine and strychnine, are complex nitrogen compounds. **Aspirin,** $C_6H_4OAc \cdot COOH$, is a derivitive of salycilic acid. **Salvarsan,** used in the treatment of syphilis, is NH_2-OHC_6H_3As-$AsC_6H_3OHNH_2$.

32. War Gases.—Chlorine, and soon after, phosgene, $COCl_2$, were employed in the World War in the earlier operations of the gas warfare; later a number of organic derivatives were used, among which were "mustard gas," $(CH_2ClCH_2)_2S$; chlorpicrin, CCl_3NO_2; "tear gas," such as brombenzyl cyanide, C_6H_5CH-BrCN; and "sneeze gas," diphenylchlorarsine, $(C_6H_5)_2AsCl$.

33. Synthetic Methanol.—In the presence of catalysts, carbon monoxide and hydrogen will combine to form a number of hydrocarbons and alcohols, or other oxidation products of hydrocarbons, for example,

$$CO + 3H_2 = CH_4 + H_2O,$$
$$CO + 2H_2 = CH_3OH,$$
$$12CO + 3H_2 = C_6H_6 + 6CO_2.$$

Of these reactions, the most important commercially is the formation of methyl alcohol, CH_3OH, or **methanol.** The reaction is favored by pressure (100–200 atmospheres are used), and the temperature range is between 300° and 600° C. Various mixed metal oxides are employed as catalysts, as, for example, copper oxide with oxides of chromium, manganese, vanadium, or zinc. Methanol is important as a solvent, and as a raw material for the synthesis of many organic compounds. It is a very satisfactory fuel for gas engines, and gives promise of becoming the motor fuel of the future.

CHAPTER XIV

SILICON

1. Silicon, the second element of Group IV, occupies as important a position in the mineral world as carbon does in the vegetable and animal. Its chemistry is characterized by the stability and complexity of the compounds of the dioxide, SiO_2, with basic oxides. In this respect, it resembles boron more closely than it does carbon. Although it forms hydrogen compounds similar to those of carbon, the bond between the silicons is readily broken, and the compounds do not possess the stability or importance of the corresponding carbon compounds. The oxide like that of boron is high melting and non-volatile, and many of its compounds are derivatives of polyacids, which resemble the boric acids. However, the majority of the silicates are salts of ortho or meta silicic acid, and thus contain the groups SiO_4 and SiO_3, the former being tetravalent and the latter divalent. Although a monoxide is known, few lower valence or unsaturated compounds have been prepared.

In connection with the resemblance between boron and silicon, reference should be made (cf. **III**—7) to the similarity in the values for the field of force about B^{+3} and Si^{+4}.

2. Occurrence.—Silicon is never found as the free element. The dioxide and its compounds constitute about 87 per cent of the earth's crust, and the element is estimated as forming 25.8 per cent of the outer portions of the earth. Silicon thus ranks next to oxygen in abundance. The principal silicon minerals are summarized in Table VI, and the important groups, such as the feldspars, pyroxenes, amphiboles, and micas, are discussed in subsequent paragraphs.

3. Elementary silicon has been prepared in a semimetallic crystalline form, and also in a so-called amorphous form. The former possesses a grey luster and fair electrical conductivity (Table I). Both forms appear, from X-ray data, to have the same atomic arrangement in the crystal, the modified diamond type, hence the amorphous form is probably a mass of very small crystals.

Amorphous silicon is prepared by the high temperature reduction of silicon halides by alkali metals, or of the dioxide by magnesium: $SiCl_4 + 4Na = Si + 4NaCl$. When the dioxide, or sodium silicofluoride, Na_2SiF_6, is reduced with excess of aluminum, the silicon dissolves in the excess metal, and upon cooling, separates in the crystalline metallic form. This may be separated from the aluminum by dissolving the latter in acid. The metallic form may also be prepared by the reduction of the dioxide with carbon in an electric furnace, although it is difficult to avoid the formation of the carbide. Amorphous silicon may be converted to the metallic form by recrystallizing from molten silver.

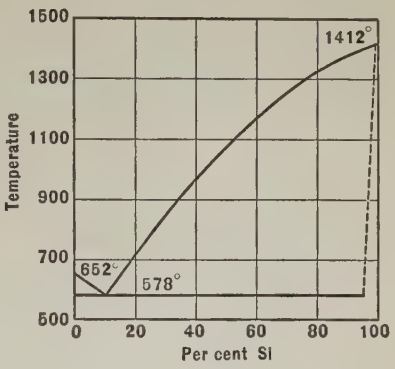


FIG. 1.—Aluminium-silicon diagram.

Silicon is of considerable importance in the steel industry. It is generally prepared, however, as ferrosilicon (Par. 6).

TABLE I

ATOMIC AND PHYSICAL PROPERTIES OF SILICON

Atomic number	14	Density (crys.)	2.4
Atomic weight	28.06	Melting point, °C	1420
Isotopes	28,29,30	Boiling point, °C	2600
Electrons in various quantum levels, 1st	2	Electrical resistivity, ohm-cm	85×10^{-3}
2d	8	Radius of Si^{+4} in crystals, cm. $\times 10^8$ (if $Cl^- = 1.81$)	0.41
3d	4		

4. Reactions of the Element.—Silicon burns in oxygen, but not readily, as a surface layer of oxide tends to stop the reaction. It ignites spontaneously in fluorine at room temperature, in chlorine at 300–350°, in bromine at 500; and the amorphous form reacts with iodine at red heat, but without luminosity. The oxidation reduction potential,

$$Si + 2H_2O = SiO_2 + 4H^+ + 4E^-: 0.6 \text{ volt},$$

is not of great significance because of the slowness of the reaction. Thus, silicon is not soluble in hydrogen ion, but due to the great stability of silicates, it does dissolve in sodium hydroxide with the evolution of hydrogen. The element is also oxidized by steam. A mixture of nitric and hydrofluoric acid gives silicon tetrafluoride. Combination occurs with nitrogen and sulfur at high temperature, and with many metals to form silicides.

TABLE II

REACTIONS OF SILICON

$Si + O_2 = SiO_2$	Not rapid
$Si + 2X_2 = SiX_4$	With halogens
$Si + 2NaOH + H_2O = Na_2SiO_3 + 2H_2$	
$Si + 2H_2O = SiO_2 + 2H_2$	With steam
$3Si + 4HNO_3 + 2HF = 3SiF_4 + 4NO + 8H_2O$	
$Si + K_2CO_3 = K_2SiO_3 + C$	Fused
$3Si + 2N_2 = Si_3N_4$	
$Si + 2S = SiS_2$	
$nSi + mM = Si_nM_m$	With many metals

5. Silicides.—Silicon dissolves in many molten metals, and the temperature-composition curves indicate the formation of both solid solutions and definite compounds. Compounds of the type, M_3Si, are formed by Li and Cu; of the type, M_2Si, by Mg, Mn, Fe, Co, Ni, and Pd; of the type, MSi, by Mn, Fe, Co, Ni, Pt, and Pd; of the type, MSi_2, by Ca, Co, Sr, V, and U; and of the type, MSi_3, by Co. A few of the more important compounds are discussed below.

6. Ferrosilicon.—FeSi is made by reducing siliceous iron ore in an electric furnace. It is employed extensively in the steel industry, especially in the manufacture of silicon steels, the more important of these being (1) acid resistant steel, e.g. "duriron" (16 per cent silicon) and (2) steel of high magnetic permeability. The addition of silicon to iron also reduces the amount of iron carbide, Fe_3C; and thus converts white cast iron into grey cast iron. Silicon added to molten steel also serves as a "deoxidizing" agent.

Hydrogenite, a mixture of ferrosilicon and solid sodium hydroxide, evolves hydrogen upon the addition of water, and has been used as a source of hydrogen for balloons and air ships.

7. Carborundum, SiC, is one of the hardest substances known. Although the data are somewhat indefinite, the arrangement of

the atoms in the crystal appears to be a modified diamond type of structure. It is manufactured extensively for use as an abrasive, by heating a core of carbon packed in sand in an electric furnace: $SiO_2 + 3C = CSi + 2CO$. The furnace is of the resistance type, the carbon core serving as the heating element.

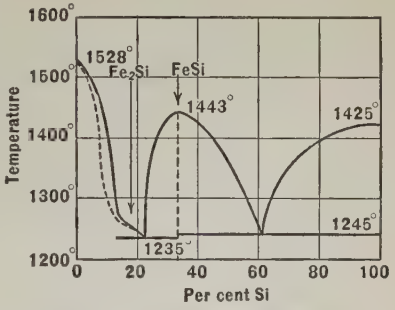


FIG. 2.—Iron-silicon diagram.

8. Calcium silicide, $CaSi_2$, is formed by heating lime, sand, and carbon in an electric furnace: $CaO + 2SiO_2 + 5C = CaSi_2 + 5CO$. It is a powerful reducing agent, and is employed as a "deoxidizing" agent in steel manufacture, and also as a reducing agent in certain explosives.

9. Silicon and Hydrogen.—The first 7 or 8 members of the series, Si_nH_{2n+2}, corresponding to the paraffin series, are known. These hydrogen compounds resemble the hydrocarbons in physical properties, but not in stability. They inflame spontaneously in air at room temperature, or slightly above, and are decomposed by cold water with the formation of silicon dioxide and hydrogen. A mixture of the various members of the series results from the action of acids upon magnesium silicide, Mg_2Si, while lithium silicide, Li_3Si, gives largely silicoethane, Si_2H_6. The existence of unsaturated hydrogen compounds is doubtful.

10. Silicon and the Halogens.—The halogens react directly with silicon, forming tetrahalides. The energy of the reaction decreases with the increasing size of the halogens; with fluorine, the reaction is spontaneous at room temperature, while with iodine the reaction occurs only at red heat. The tetra halides hydrolyze in water to form silicic acid and the hydrogen halide, and this hydrolysis is complete with all the tetrahalides, except the **tetrafluoride.** Due to the stability of the fluoride, silicon dioxide and the mineral silicates dissolve in hydrogen fluoride: $SiO_2 + 4HF = SiF_4 + 2H_2O$. The solid tetrafluoride sublimes without melting; but under a pressure of 2 atmospheres it melts at $-77°$. At room temperature the tetrafluoride is a gas with a pungent odor. With water, partial hydrolysis results in the

formation of **fluosilicic acid**: $3SiF_4 + 3H_2O = 2H_2SiF_6 + H_2SiO_3$. This is a moderately strong acid, and its potassium salt is but slightly soluble. X-ray data on the solid fluosilicates show that the six fluorine atoms are arranged symmetrically at equal distances about the silicon atom. In the acid nature of the fluoride, silicon again resembles boron.

11. Silicon tetrachloride is prepared by the action of chlorine on silicon carbide, or on a hot mixture of silica and carbon: $2Cl_2 + SiC = SiCl_4 + C$; $SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO$. The product prepared by these reactions also contains higher members of the series, Si_nCl_{2n+2}. Mixtures of the tetrachloride and ammonia have been employed for the preparation of military smoke screens, since in moist air solid silicic acid and ammonium chloride are formed. With sulfur trioxide, the oxychloride, Si_2OCl_6, and also silicon dioxide results: $2SiCl_4 + 2SO_3 = Si_2OCl_6 + S_2O_5Cl_2$, and $SiCl_4 + 3SO_3 = SiO_2 + 2S_2O_5Cl_2$.

12. By the action of hydrogen chloride upon heated silicon, chlorine hydrosilicons are formed, the most important being **silicochloroform**, $SiHCl_3$. This and other silicon hydrogen halides hydrolyze in water with the formation of oxyhydrogen compounds: $2SiH_3Cl + H_2O = 2HCl + 2(SiH_3)_2O$ (Disiloxan): $SiH_2Cl_2 + H_2O = 2HCl + (SiH_2)O$ (Prosiloxan): $Si_2Cl_6 = 4H_2O = 6HCl + (SiO_2H)_2$ (Silico-oxalic acid).

Silicon and Oxygen

13. Silicon Monoxide.—The yellowish brown monoxide, SiO, may be prepared by the reaction between carbon and excess silicon dioxide at temperatures around 2000°. $SiO_2 + C = SiO + CO$. The oxide is a solid at these temperatures, and unless rapidly cooled, decomposes: $2SiO = Si + SiO_2$. It is used commercially under the name **monox**, as a pigment, and also as an abrasive.

14. Silicon Dioxide.—Free silica, SiO_2, constitutes about 12 per cent of the earth's crust; and this, together with silica in combination with basic oxides, approximately 60 per cent. It occurs in three crystalline forms, quartz, tridymite, and cristobalite, and each of these has a number of modifications (Table III). It also exists as the supercooled liquid, or quartz glass. Sand, flint, and agate are familiar forms of silica. Kieselguhr, or diatomaceous earth, is silica resulting from the skeletons of diatoms.

Quartz belongs to the hexagonal system with threefold symmetry about its principal axis. The crystal has no plane or center of symmetry; and therefore exists in two forms called "right-handed" and "left-handed," which are mirror images of each other and rotate the plane of polarized light in opposite directions (Fig. 3). Crystals of enormous size are occasionally found in nature. Quartz has a density of 2.65, and is somewhat harder than ordinary glass. It is very transparent over a range of wave-lengths extending from the infra-red far into the ultra-violet (transmission for 1 mm. thickness = 67 per cent at 0.19 μ), and therefore finds considerable application in the manufacture of optical instruments and ultra-violet lamps.

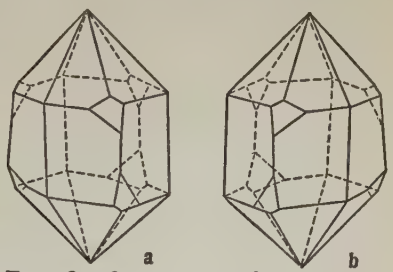


FIG. 3.—Quartz crystals; a, right-handed; b, left-handed.

As indicated in Table III, tridymite and cristobalite are unstable with respect to quartz at ordinary temperatures. The transition is slow at low temperatures, however, and both forms are found in nature, especially in lavas which have cooled quickly.

TABLE III

MODIFICATIONS OF SILICA

	Crystal System	Specific Gravity	Transition Temperature, °C.
α-Quartz	Hexagonal	2.65	575, to β-Quartz
β-Quartz	Hexagonal	2.63	870, to β_2-Tridymite
α-Tridymite	Rhombic ?	2.28	117, to β_1-Tridymite
β_1-Tridymite	Hexagonal		163, to β_2-Tridymite
β_2-Tridymite	Hexagonal		1470, to β-Cristobalite
α-Cristobalite	Tetragonal	2.35	225, to β-Cristobalite
β-Cristobalite	Cubic	2.21	1710, to liquid
Silica glass	Amorphous	2.21	

Liquid silica is highly viscous, and like all such liquids, readily supercools. Quartz glass has a lower density (2.2) than the crystals, and a very small coefficient of expansion, 0.0_654 (linear). Because of its low expansion, it is possible to plunge white hot

quartz glass into water without having it crack. Quartz glass does not soften below 1500°, whereas ordinary glass softens around 600 to 900°. Both of these qualities make it very valuable in the construction of apparatus for high temperature measurements. It should be noted, however, that helium and hydrogen diffuse rather readily through quartz glass at temperatures as low as 300°. Quartz glass is now manufactured by fusing pure silica in a high temperature furnace.

The various forms of silica are soluble in alkalies with the formation of silicates, but they are only slightly affected by acids, except hydrofluoric which converts silica into the tetrafluoride. The great stability of silicon dioxide is related to its high heat of formation: $Si + O_2 = SiO_2 + 191{,}000$ cal. It is exceeded by that of the fluoride, however: $Si + 2F_2 = SiF_4 + 220{,}000$ cal.

15. Silicic Acids.—The result of the addition of a strong acid to a soluble silicate is the formation of a colloidal solution, or hydrogel, of the general formula, $mSiO_2 \cdot nH_2O$. Upon heating, the gel may be gradually dehydrated and the dioxide formed. Partially dehydrated gels have high absorbent power, and are now used commercially in the absorption of benzene, sulfur dioxide, nitric acid, nitrogen dioxide, and other vapors. Many forms of hydrated silica occur in nature, such as opal.

Salts and mineral derivatives of a large number of silicic acids are known. The nomenclature of these hypothetical acids is indicated in Table IV.

TABLE IV

Silicic Acids

	Mono- $mH_2O \cdot SiO_2$	Di- $mH_2O \cdot 2SiO_2$	Tri- $mH_2O \cdot 3SiO_2$	Tetra- $mH_2O \cdot 4SiO_2$
Ortho-	H_4SiO_4	$H_6Si_2O_7$	$H_8Si_3O_{10}$	$H_{10}Si_4O_{13}$
Meta-	H_2SiO_3	$(H_2SiO_3)_2$	$(H_2SiO_3)_3$	$(H_2SiO_3)_4$
Meso-	——	$H_2Si_2O_5$	$H_4Si_3O_8$	$H_6Si_4O_{11}$
Para-	——	——	$H_2Si_3O_7$	$H_4Si_4O_{10}$
Tertero-	——	——	——	$H_2Si_4O_9$

16. Alkali Silicates.—Commercial sodium silicate, known as **water glass,** is made by fusing sand, flint, or kieselguhr with sodium carbonate and charcoal, and extracting the glassy mass

in an autoclave, or by dissolving the silica in sodium hydroxide. The product has a ratio of SiO_2 to Na_2O, between 2 and 4, and is usually sold in concentrated solution as a syrupy liquid.

Water glass is used in soaps and washing powders to provide an alkaline reaction. It is used: for fireproofing materials; in paper manufacturing as sizeing; as an egg-preservative; and as a mineral glue for cementing wood, glass, porcelain, etc.

The other alkali silicates resemble the sodium compound. Temperature-composition curves for the system, K_2O-SiO_2-H_2O, show many hydrates of the salts, K_2SiO_3 and $K_2Si_2O_5$, and lithium forms the ortho salt, Li_4SiO_4. Although silica is soluble in concentrated ammonia, solid ammonium silicates cannot be prepared, as the solutions hydrolyze completely when evaporated.

17. Mineral Silicates.—Rocks may be classified as (1) igneous, (2) sedimentary, (3) metamorphic. Igneous rocks have resulted from the solidification of the earth's molten magma. Sedimentary rocks are formed from the igneous by the action of weathering agents, followed by sedimentation under water, e.g. sandstone. Certain igneous and sedimentary rocks have been subjected to heat, pressure, or solvent action, and are thereby modified to form the metamorphic rocks, e.g. serpentine.

Analysis of a number of the more common igneous rocks gives the ranges in composition summarized in Table V for the component oxides:

TABLE V

Composition of Igneous Rocks

Oxide.....	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	H_2O
Per cent....	40–75	7–18	0.2–8	0.3–14	0.1–24	0.2–15	1–5	1–8	0.5–4

The most abundant igneous rock is **granite,** a mixture of feldspar (Table VI), mica, and quartz. **Rhyolite** and **obsidian** have the same general composition as granite, but the former has cooled much more rapidly and its individual crystals are much smaller than those in granite. Obsidian is a volcanic glass. Next to granite, the most important igneous rocks are the ferromagnesium silicates, the pyroxenes, and amphiboles.

18. Feldspar is the most abundant of all minerals. Crystal structure data indicate that the formula of the alkali feldspars should be written $KAlSi(SiO_4)_2$. The sodium and calcium

feldspars are isomorphous, and the general formula might be written as $[(NaAlSi)(CaAl_2)](SiO_4)_2$. Large quantities of feldspar are used in the ceramic industries (see Pottery). Feldspar is converted by the action of carbon dioxide and water into (1) mica or by further action into (2) kaolinite (clay): (1) $3KAlSi_3O_8 + H_2CO_3 = KH_2Al_3Si_3O_{12} + 6SiO_2 + K_2CO_3$; (2) $2KAlSi_3O_8 + 2H_2O + CO_2 = H_4Al_2Si_2O_9 + K_2CO_3 + 4SiO_2$.

19. The **micas** are acid orthosilicates of aluminum with magnesium, ferrous iron, and the alkalies. Their most striking characteristic is cleavage into very thin elastic transparent sheets. Mica is used extensively in the electrical industries as an insulator. It is used in making windows for stoves, in lamp chimneys, as Christmas tree "snow," as a decorative material for wall paper, and in many special paints. When heated, mica breaks down into **leucite**: $KH_2Al_3(SiO_4)_3 = KAl(SiO_3)_2 + Al_2O_3 + SiO_2 + H_2O$.

20. The term **asbestos** includes several of the magnesium silicates, e.g. **amphibole** and **olivine.** These minerals have a fibrous structure, silky luster, and are difficultly fusible. Asbestos is important commercially as a thermal insulator. The long fibers permit the manufacture of asbestos yarn, cloth, and paper, and from these innumerable fireproof objects. Mixtures of asbestos and Portland cement are used in fireproof shingles.

21. Kaolin, impure kaolinite, or **clay,** is a hydrated aluminum silicate, and **talc,** or **soapstone,** is a hydrated magnesium silicate. Clay is further discussed under pottery. Talc is used in soap, French chalk, talcum powder; and in paint, roofing, and rubber. A fibrous form is used extensively in paper. Soapstone is used as a refractory material.

TABLE VI

MINERAL SILICATES

Feldspars	Orthoclase, $KAlSi_3O_8$ (monosymmetric) Microcline, $KAlSi_3O_8$ (anorthic) Anorthoclase, $NaAlSi_3O_8$ (anorthic) Plagioclase, $n(NaAlSi_3O_8)m(CaAl_2Si_2O_8)$
Feldspathoid group	Leucite, $KAl(SiO_3)_2$ Nepheline, $[Na, K]AlSiO_4{}^{\circ}n(NaAlSi_3O_8)$ Sodalite, $Na_4Al_3Cl(SiO_4)_3$ Lazurite, $Na_5Al_3S(SiO_4)_3$

TABLE VI (Cont'd)

MINERAL SILICATES (Cont'd)

Pyroxene (Cleavage 87° and 93°)	Enstatite, $MgSiO_3$
	Hypersthene, $[Mg, Fe]SiO_3$
	Diopside, $Ca[Mg, Fe](SiO_3)_2$
	Augite, $CaMg(SiO_3)_2 + [Mg, Fe][Al_2O_3, Fe_2O_3](SiO_3)$
	Wollastonite, $CaSiO_3$
Amphibole (Cleavage 56° and 124°)	Rhodonite, $MnSiO_3$
	Anthophyllite, $[MgFe]SiO_3$
	Tremolite, $Ca[Mg, Fe]_3(SiO_3)_4$
	Hornblende, $Ca[Mg, Fe]_3(SiO_3)_4 + [Al, Fe][F, OH]SiO_3$
	Glaucophane, $NaAl(SiO_3)_2 \cdot [Fe, Mg]SiO_3$
Complex calcium aluminum silicates	Vesuvianite, $Ca_6Al_2[OH, F](SiO_4)_5$
	Epidote, $Ca_2(Al, Fe)_3OH(SiO_4)_3$
	Prehnite, $H_2Ca_2Al_2(SiO_4)_3$
	Scapolite, $Ca_4Al_2(CO_3)(SiO_4)_2$ to $Na_4AlClSi_3O_8$
Mica	Muscovite, $H_2KAl_3(SiO_4)_3$
	Biotite, $(HK)_2[Mg, Fe]Al_2(SiO_4)_3$
	Phlogopite, $H_2KMg_3Al(SiO_4)_3$
	Lepidolite, $Li_2[F, OH]_2Al_2(SiO_3)_3$.
Zeolites	Heulandite, $H_4CaAl(SiO_3) \cdot 3H_2O$
	Stilbite, $H_4[Ca, Na]Al_2(SiO_3)_6 \cdot 4H_2O$
	Chabazite, $[Ca, Na_2]Al_2(SiO_3)_4 \cdot 6H_2O$
	Analcite, $NaAl(SiO_3)_2 \cdot H_2O$
	Natrolite, $Na_2Al_2Si_3O_{10} \cdot 2H_2O$
Chlorites	Biotite-Chlorite, $[Al, Fe][H, MgOH, FeOH, Al(OH)_2]_6$-$Al(SiO_4)_3$
	Phlogopitic-Chlorite, $[H, Mg(OH), FeOH, Al(OH)_2]_9$-$Al(SiO_4)_3$
Miscellaneous Metasilicates	Chrysocolla, $CuSiO_3 \cdot 2H_2O$
	Talc, $H_2Mg_3(SiO_3)_4$
	Kaolinite, $H_4Al_2Si_2O_9$
	Serpentine, $H_4Mg_3Si_2O_9$
	Beryl, $Be_3Al_2(SiO_3)_6$
	Spodumene, $LiAl(SiO_3)_2$
	Calamine, $Zn_2(OH)_2SiO_3$
Miscellaneous Orthosilicates	Willemite, Zn_2SiO_4
	Zircon, $ZrSiO_4$
	Andalusite, $(AlO)AlSiO_4$
	Kyanite, $(AlO)AlSiO_4$
	Sillimanite, $(AlO)AlSiO_4$
	Topaz, $[AlF_2, Al(OH)_2]AlSiO_4$
	Titanite, $Ca(TiO)SiO_4$
Borosilicates	Tourmaline, $R_9Al_3(B_2O_3)(OH)_2(SiO_4)_4$
	Datolite, $CaB(OH)SiO_4$
	Axinite, $HCa_2(Fe, Mn)Al_2B(SiO_4)_4$
Garnet	Grossularite, $Ca_3Al_2(SiO_4)_3$
	Almandite, $Fe_3Al_2(SiO_4)_3$
	Pyrope, $Mg_3Al_2(SiO_4)_3$
	Andradite, $Ca_3Fe_2(SiO_4)_3$
Olivine group	Olivine, $(Mg, Fe)_2SiO_4$
	Forsterite, Mg_2SiO_4

22. Pottery and Porcelain.—Mixtures of clay (kaolinite), quartz, and feldspar, in various proportions and baked at various temperatures, form an extensive series of ceramic products. Most types of pottery or bricks are made from naturally occurring clays, which contain sand and feldspar. They are usually colored buff or red by iron oxide, the white porcelain clays being relatively scarce. Upon heating, kaolin is altered, probably losing water, according to the equation: $H_4Al_2Si_2O_9 = Al_2SiO_5 + SiO_2 + 2H_2O$; and around 1200° the feldspar fuses and serves to bind the clay and quartz together. The properties of the earthenware depend to a great extent upon the temperature at which it is baked, and there is often but slight variation in composition between different types of products. Soft porcelain contains a high per cent of calcium phosphate. Glaze is imparted to the cheaper grades of pottery by the introduction of sodium chloride near the end of the firing. Other glazes used are fusible lead calcium alumino-borosilicates, or, in many cases, simple feldspar.

23. Glass.—Glass is a fused non-crystalline mixture of basic oxides and silicon dioxide. The basic oxides are usually the alkalies and alkaline earths, but they may be substituted in whole or in part by oxides of lead, zinc, arsenic, antimony, aluminum, etc.; and the silicon dioxide by boric or phosphoric oxides. Like all super-cooled liquids, glass does not have a definite melting point, but softens gradually over a range of temperatures. In this viscous state, glass may be blown or rolled into almost any desired shape or form. The raw materials which are fused together to form glass are sand, or the other acid oxides, and generally the carbonates of the basic constituents.

The manufacture of common **soda glass** is often represented by the equation, $2Na_2CO_3 + CaCO_3 + 6SiO_2 = Na_4CaSi_6O_{15} + 3CO_2$, but the product cannot be considered as a definite compound. It is used in making bottles, window glass, glass tubing, etc. The composition of soda glass is approximately: SiO_2, 71–78 per cent, Na_2O, 12–17, CaO, 5–15, Al_2O_3, 1–4. The corresponding **potash glass,** also called **hard glass,** or **Bohemian glass,** has a higher fusing temperature. **Potash-lead** glass, or **flint glass,** has a high density and index of refraction, and is used in making cut glass articles. **Pyrex** glass is very high in the acid oxides: SiO_2, 80 per cent, B_2O_3, 12 per cent, with the

balance Na_2O and Al_2O_3. It has a low coefficient of expansion, and is, therefore, very suitable for articles subject to sudden changes in temperature. It is also resistant to chemical action. Jena glass is a zinc-barium borosilicate.

Glass may be colored by the presence of small amounts of metal oxides: chromium or copper giving green; cobalt, blue; manganese, violet. A colloidal metal suspension of gold gives ruby glass. "Milk glass" usually contains stannic oxide or calcium fluoride.

If glass is held at a high temperature for a long time, a certain amount of crystallization may occur (called devitrification). Thick glass objects must be carefully annealed, i.e. cooled very slowly, as the cooling of the outer portions more rapidly than the interior will result in great strains and the subsequent cracking of the object.

24. Portland Cement.—Although lime mortars have been used for centuries, the modern hydraulic cement dates back only to about 1825, and its extensive use to about 1900. The approximate composition of Portland cement is given in Table VII.

TABLE VII

Composition of Portland Cement

Oxide.....	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O, K_2O
Per cent.....	58–67	19–26	4–11	2–5	0–5	0–2.5	0–3

Cement is made by heating a mixture of limestone and clay, or material of equivalent composition, to the point of incipient fusion (about 1450° C.). The product, termed clinker, is ground with 2–3 per cent of gypsum, added to decrease the time of setting, to give the cement.

The chemical composition appears to be largely the three compounds, Ca_2SiO_4, Ca_3SiO_5, and $Ca_3(AlO_3)_2$. Setting occurs upon the addition of water, and is due to the hydration of these compounds. In this action, the tricalcium silicate appears to be especially important, as it forms gelatinous hydrates which gradually harden and cement the crystals together.

The production of cement in the United States in 1925 was about 150 million barrels. The major portion of this was used in mixture with crushed rock and sand to make concrete.

25. Silicate Analysis.—In detecting the presence of silicon, advantage is taken of the volatility of silicon tetrafluoride. The sample is heated with hydrofluoric acid in a lead or platinum dish. If silicon is present, a drop of water in a wire loop, placed in the fumes, becomes cloudy owing to the formation of silicic acid: $3SiF_4 + 3H_2O = H_2SiO_3 + 2H_2SiF_6$.

Silicates are determined quantitatively by gravimetric methods, generally separating silicon dioxide and weighing as such. In this process, decomposition of the silicate may often be accomplished by digesting with concentrated hydrochloric acid, leaving a residue of silica. Other silicates must first be fused with sodium carbonate before they can be decomposed by acid. The silica residue may be contaminated with $BaSO_4$, Al_2O_3, Fe_2O_3, TiO_2, and oxides of certain rare elements; the amount in the mixture is often determined by heating with hydrofluoric acid, obtaining the silica by loss of weight, due to the volatilization of the tetrafluoride.

CHAPTER XV

THE METALS OF GROUP IV. TITANIUM, ZIRCONIUM, HAFNIUM, THORIUM AND GERMANIUM, TIN, LEAD

1. The first and second elements of Group IV, carbon and silicon, have been discussed in the two preceeding chapters. The remaining elements of the main group are titanium, zirconium, hafnium and thorium, and of the subgroup, germanium, tin and lead. All of the free elements are metals but both branches of the group show many similarities to silicon in their chemical properties.

Titanium and the heavier elements of the main group are each the second elements of a transition series in which the kernel is being transformed from the noble gas structure to the eighteen electron type (Appen. XVIII), and, instead of having four electrons in the outer quantum level, they appear to have but two. However, the two electrons which have dropped back to a lower level are easily removed so that all members of the group show the characteristic valence of + 4. Titanium has also a fairly stable trivalent and a less stable divalent state.

The subgroup elements show valences of both + 2 and + 4, the former becoming increasingly stable with respect to the latter with increasing atomic weight.

The tetroxides of all the elements, except thorium, are amphoteric, and those of the main group are, in general, somewhat more basic than the oxides of the corresponding elements of the subgroup, which is in agreement with a slightly larger size of the main group ions, and in both groups the basic character increases with increasing size. Like silicon, all of the members of the group form complex fluorides, and all the tetrachlorides, except thorium, are volatile liquids.

One of the most striking differences between the two branches of the group is the much greater stability of the sulfides of germanium, tin and lead. This stability of the sulfides is a general characteristic of the ions with eighteen electrons in the outer shell of the kernel (cf. VII—2). The elements of Subgroup

IV resemble those of Subgroup III in not forming complex ions with ammonia.

Cerium is often discussed in connection with Group IV, but it has been included in the rare earths, although it does form a dioxide which resembles in many respects the dioxides of zirconium and thorium.

TITANIUM, ZIRCONIUM, HAFNIUM, AND THORIUM

2. Occurrence.—The elements of this group are by no means as rare as they have commonly been considered. Titanium ranks tenth among the elements in order of abundance, the per cent of the element present in the earth's crust being estimated at 0.43. The values for the other elements of the group are: zirconium, 0.02; hafnium, 0.002; and thorium, 0.002.

The elements do not occur free, but their compounds are widely distributed in nature, although, as a rule, extensive deposits of comparatively pure mineral are not common. Due to the similarity in chemical behavior between these elements and silicon, their presence in rocks is often overlooked.

The most important titanium ores are **rutile,** TiO_2, and **ilmenite,** $FeTiO_3$. Metatitanates of ferric iron, calcium, magnesium, manganese, and lead, also occur. Titanosilicates such as **sphene,** $CaTiSiO_5$, are common, and less frequently borotitanates and titanoantimonates.

Zirconium occurs principally as **baddeleyite,** ZiO_2, and **zircon,** $ZrSiO_4$, the most extensive deposits being located in Brazil. Complex zirconates, often containing the other members of the group, are also found. Hafnium is present to the extent of 1 or 2 per cent in practically all primary zirconium minerals. Thorium orthosilicate, $ThSiO_4$, or possibly $ThO_2 \cdot SiO_2$, occurs as the black mineral **thorite** and also as the orange colored mineral **orangite.** These thorium ores and also the mineral **thorianite,** ThO_2, frequently contain uranium oxides, UO_2 and U_2O_3. The principal source of commercial thorium is monazite sand (see Rare Earths).

3. The Metals.—The electro-positive nature of the elements, together with their great tendency to form carbides, nitrides, and silicides at high temperatures, renders the preparation of the metals extremely difficult. The reduction of the chlorides or potassium complex fluorides by heating with sodium in steel

bombs gives a comparatively pure product. The Goldschmidt reduction with aluminum gives aluminum alloys. In the case of titanium, the alloy contains 5 or 6 per cent aluminum, but

TABLE I

Atoms and Physical Properties

	Ti	Zr	Hf	Th
Atomic weight...	47.90	91.22	178.6	232.15
Atomic number..	22	40	72	90
Isotopes.....	None	90, 94, 92	?	228, 230, 232, 234
Electrons in various quantum levels, 1st.....	2	2	2	2
2d.....	8	8	8	8
3d.....	8 (10)	18	18	18
4th....	4 (2)	8 (10)	32	32
5th....		4 (2)	8 (10)	18
6th....			4 (2)	8 (10)
7th....				4 (2)
Melting point, °C.	1800	1700	1700	1845
Boiling point, °C.	>3000	>2900	>3200	>3000
Density.....	4.5	6.4	11.4	11.2
Electrical resistivity, ohm-cm.	3×10^{-6}	170×10^{-6}		18×10^{-6}
Radius of M^{+4} ion in crystals, cm. $\times 10^{8}$ (if $Cl^{-} = 1.81$) ...	0.68	0.80	——	1.02

if iron is present, the product is largely ferro-titanium. Zirconium may be separated from the aluminum alloy by distillation. The reduction of titanium dioxide by carbon in an electric furnace yields a mixture of the metal and carbide. Ferro-carbon-titanium is made by the reduction of mixtures of iron and titanium oxides. Thorium is best prepared by reduction of the dioxide with calcium in the presence of calcium chloride in a bomb.

The metals are described as hard and brittle, though these properties may be due, in part, to the presence of impurities. The metals titanium, zirconium, and hafnium appear to have the hexagonal close packed form of crystal lattice, while thorium has a face centered cubic lattice. Titanium is almost as good an electrical conductor as aluminum.

There are practically no commercial uses of the pure metals. Iron-titanium alloys are used extensively in the steel industry; the titanium is considered extremely valuable in removing nitrogen (by forming nitride) from, and in imparting toughness to steel.

4. Reactions of the Metals.—The reactions of the metals are summarized in Table II. At ordinary temperatures, they are not very reactive, being oxidized but slowly by oxygen or by hydrogen ion. Measurements of the electrode potentials of the group are unreliable because of the difficulties in obtaining equilibrium conditions. The potentials given in Table II have been calculated from the following heats of formation (kg. cal.): TiO_2, 215; ZrO_2, 177; ThO_2, 326, and the necessary entropy values.

TABLE II

REACTIONS OF Ti, Zr, Hf AND Th

$M + O_2 = MO_2$	Burn when heated
$M + 2X_2 = MX_4$	With halogens when heated
$M + 2H_2O = MO_2 + 2H_2$	With steam
$M + 4HF + MF_4 + 2H_2$	Not rapid with Th
$M + 4HCl = MCl_4 + 2H_2$	With hot concentrated acid, but Ti gives $TiCl_3$
$M + H_2 = MH_2$	TiH_2 doubtful. Th gives ThH_4
$M + 2S = MS_2$	Also react with P, C, B, and Si at high temperatures
$3M + 2N_2 = M_3N_4$	Also MN
$M + 2H_2O = MO_2 + 4H^+ + 4E^-$	Potential in volts, Ti, 0.9; Zr, 0.5; Th, 2.1

TITANIUM COMPOUNDS

5. Valence States.—Titanium forms compounds in which it has the valences of + 2, + 3, and + 4. Important oxidation-reduction potentials relating the valence states are given below:

	Volts
$Ti^{++} = Ti^{+++} + E^-$	0.37
$Ti^{+++} = Ti^{++++}$ (or TiO^{++}) $+ E^-$	− 0.04
$Ti(OH)_3 + OH^- = TiO_2 + 2H_2O + E^-$	*ca* 1.0

6. Divalent Titanium.—The **oxide,** TiO, is prepared by the high temperature reduction of the dioxide by carbon or magnesium. It is basic but its salts are readily oxidized in solution by hydrogen ion unless the acid concentration is very low. The **dichloride** may be formed at high temperatures by the decomposition of the trichloride: $2TiCl_3 = TiCl_2 + TiCl_4$.

7. Trivalent Compounds.—The **sesquioxide** is formed in the reaction: $2TiO_2 + H_2 = Ti_2O_3 + H_2O$. It also is basic. The corresponding **titanous hydroxide,** $Ti(OH)_3$, is precipitated upon the addition of alkalies to titanous salts in solution. This hydroxide is a very powerful reducing agent (Par. 5). It evolves hydrogen to form the dioxide: $Ti(OH)_3 = TiO_2 + H_2O + \frac{1}{2}H_2$; and reduces nitrate in alkaline solution to ammonia: $8Ti(OH)_3 + NO_3^- = NH_3 + 8TiO_2 + OH^- + 10H_2O$. Anyhydrous **trihalides** may be prepared by reducing the tetrahalides at moderately high temperatures, e.g. $TiCl_4 + Ag = TiCl_3 + AgCl$.

Solutions of titanous ion, Ti^{+++}, are readily prepared from solutions of titanic salts by electrolytic reduction, or by the reducing action of zinc upon the hot solution. Titanous solutions are violet. Titanous solutions are important as volumetric reagents, as they are oxidized quantitatively by many oxidizing agents, e.g. Fe^{+++} and MnO_4^-. Titanous ion is much less hydrolyzed than the tetravalent ion. The formation of the slightly soluble hydroxide has been discussed above. The cesium titanous alum, $CsTi(SO_4)_2 \cdot 12H_2O$, is but sparingly soluble.

8. Tetravalent Compounds.—The **dioxide** occurs in nature in two tetragonal forms, **rutile** and **anatase,** and also in a rhombic form called brookite. The pure oxide is white, but natural rutile is usually brown or black. The arrangement of the atoms in the rutile crystal lattice is given in Appendix V. This is the common crystal form of compounds MX_2 when the ratio of the diameter of M to X is 0.6. When this ratio is greater, the arrangement is generally that of fluorite.

The fused oxide is difficult to dissolve, but the hydrated forms dissolve readily in acids and slightly in alkalies. However, the chemistry of the titanium minerals is essentially that of an acid oxide. The oxide fused with metal oxides or carbonates yields **titanates,** e.g. $CaTiO_3$, $Ba_2Ti_3O_8$, $ZnTiO_3$, Zn_2TiO_3, $PbTiO_3$, Mn_2TiO_4. The potassium metatitanate, K_2TiO_3, is soluble in cold water, but upon boiling, the titanium is completely precipitated as the dioxide.

When an acid solution of a titanium salt is made alkaline, a hydrogel is formed, resembling that of silica. The orthoacid, H_4TiO_4, is said to be precipitated in cold, and the metatitanic-acid, H_2TiO_2, in hot solutions.

The addition of hydrogen peroxide to a solution of the sulfate

yields **peroxytitanic** acids for which the formulae, H_2TiO_4 and H_4TiO_5, have been written.

9. The anhydrous **halides** are prepared by direct reaction of the elements, or by the action of the halogen upon heated mixtures of the oxide and carbon, e.g. $TiO_2 + C + 2Cl_2 = TiCl_4 + CO_2$. Water solutions are prepared by dissolving the hydrated oxide in concentrated hydrohalic acid, but in dilute acid the halides readily hydrolyze to the dioxide. The lighter halides form complex ions, e.g. TiF_6^{--} and $TiCl_6^{--}$. **Potassium fluorotitanate,** K_2TiF_6, is but slightly soluble.

10. The hydrated **dioxide** dissolves in sulfuric acid solutions. In dilute acid, the sulfate hydrolyzes to form **basic sulfates,** e.g. $Ti_2O(SO_4)_3 \cdot 3HO$ and $TiO \cdot SO_4 \cdot nH_2O$. Similarly **basic nitrates** and **phosphates** exist, and the phosphates form a number of double basic compounds, e.g. potassium titanyl phosphate, $K(TiO)PO_4$.

The addition of soluble sulfides to titanium solutions results in the precipitation of the dioxide, but the **sulfide** may be formed by heating chloride and hydrogen sulfide vapors together: $TiCl_4 + 2H_2S = TiS_2 + 4HCl$. The sulfide does not form polysulfides with alkali sulfides. At high temperatures, the element unites with sulfur forming TiS and Ti_2S_3.

Zirconium Compounds

11. Zirconium forms the **dioxide** and possibly two oxides of lower valence, but the evidence in favor of these is of doubtful nature. The dioxide occurs in nature as the mineral baddeleyite. Like titania, it reacts with fused hydroxides and carbonates, forming insoluble **zirconates,** e.g. Na_2ZrO_3, $CaZrO_3$, $PbZrO_3$. The hydrated oxide, usually regarded as **zirconium hydroxide,** $Zr(OH)_4$, is formed as a **hydrogel** upon the addition of alkali to solutions of zirconium salts. The hydroxide is readily soluble in acids and somewhat soluble in cold concentrated alkali, with which it reacts mainly to form insoluble zirconate. Hydrogen peroxide reacts with the hydroxide to form the **hydrated peroxide,** probably H_4ZrO_5.

The **tetrahalides** resemble those of titanium in properties and methods of formation. Basic halides are obtained upon evaporation of the water solutions of the halides, e.g. **zirconyl chloride,** $ZrOCl_2$. Many slightly soluble **fluorozirconates** are known, e.g. K_2ZrF_6, $BaZrF_6$, and also less stable **chlorozirconates.**

Reduction of the tetrachloride with aluminum at 300° yields the **trichloride,** $ZrCl_3$, and at higher temperatures, the **dichloride,** $ZrCl_2$, but these compounds cannot be formed in water solutions.

Zirconium sulfides, sulfates, nitrates, and **phosphates,** resemble closely the corresponding titanic compounds. The normal sulfate may be crystallized from concentrated sulfuric acid solutions, and many basic and double sulfates are known. Hydrogen reacts with zirconium at red heat, apparently forming the unstable **hydride,** ZrH_2.

Hafnium Compounds

12. Hafnium resembles zirconium so closely that the presence of several per cent of hafnium in the zirconium compounds was not discovered until 1923, although the chemistry of zirconium was carefully investigated during the preceeding century. Any compound formed by the one element appears to be formed by the other, and, as a rule, the melting points, boiling points, and solubilities of the two compounds are very similar. Hafnium dioxide and hydroxide appear to be slightly more basic than the zirconium compounds.

Thorium Compounds

13. Thorium **dioxide,** or **thoria,** appears to possess no acid properties, even when fused with alkali, and in this respect differs from the other members of the group. The unhydrated oxide dissolves but slowly in acids, but the hydrated form, $ThO_2 \cdot 2H_2O$, or thorium **hydroxide,** $Th(OH)_4$, is readily soluble in acids. The hydroxide is formed as a gelatinous precipitate upon the addition of alkali hydroxides or ammonia to thorium salts in solution. Lower oxides have not been prepared, but a hydrated **peroxide** is formed by the action of hydrogen peroxide upon the hydroxide.

Mixtures of thorium and cerium dioxides, heated to a high temperature, exhibit a brilliant white luminescence, the maximum emissivity being obtained with about 1 per cent of cerium dioxide. Advantage is taken of this fact in the **Welsbach gas mantles,** which are manufactured by saturating fabric with the nitrates of these metals. When ignited, the oxide residue retains the shape of the original fabric. A few per cent of beryllium and magnesium nitrates are usually added to give the ash greater strength.

The **tetrahalides** are prepared by methods characteristic of the group. The **fluoride,** ThF_4, and its hydrate, $ThF_4 \cdot 4H_2O$, are very slightly soluble, as is also the **potassium fluorothorate,** $K_2ThF_6 \cdot 4H_2O$. Various hydrates of the **tetrachloride** may be crystallized from aqueous solution, providing sufficient acid is present to prevent the precipitation of **basic chlorides.** Lower valent halides have not been prepared. The **sulfide** may be made by the action of sulfur or hydrogen sulfide upon the heated metal. It is not stable in water solutions. The anhydrous **sulfate** is very hygroscopic and forms hydrates containing 9, 8, 6, 4, and 2 moles of water. The **nitrate,** $Th(NO_3)_4 \cdot 12H_2O$, may be crystallized from concentrated acid solutions, and the phosphate, $Th_3(PO_4)_4 \cdot 4H_2O$, is formed as a gelatinous precipitate by adding sodium phosphate to a solution of a thorium salt. Both the nitrate and phosphate form many double salts, e.g. $KTh(NO_3)_5 \cdot 9H_2O$, and $NaTh_2(PO_4)_3$. Normal thorium carbonate has not been prepared, but a number of **basic carbonates** and **complex carbonates** are known, e.g. $ThO \cdot CO_3 \cdot 2H_2O$, and $(NH_4)_2$-$Th(CO_3)_3 6H_2O$. The basic carbonates are soluble in excess ammonium carbonate, probably with the formation of complex carbonate. The **iodate,** $Th(IO_3)_4$, is but slightly soluble and resembles the corresponding ceric compound.

14. Analytical.—Titanium may be extracted from its ores by alkaline fusion, followed by digestion in acid, or by fusion with potassium acid sulfate and extraction with water. The addition of hydrogen peroxide to a sulfuric acid solution of titanium produces the characteristic yellow or orange color of the peroxyacid. Tetravalent titanium may be reduced to the violet trivalent state by zinc in hot acid solution, and the titanium may be determined quantitatively by titrating this solution with permanganate. Titanium hydroxide is precipitated by the addition of alkalies, ammonia, and soluble carbonates and sulfides to solutions of titanium salts. If formed in cold solution, it is readily soluble in acids, and somewhat soluble in excess alkali. Precipitated from hot solution, it is not rapidly soluble in acid.

Zirconium and hafnium ores may be got into solution by methods similar to those given for titanium. The two elements may be separated from iron, aluminum, beryllium, titanium, and thorium by precipitation from highly acid solutions, as the very slightly soluble zirconyl and hafnyl phosphates, $ZrO(H_2PO_4)_2$.

Alkalies precipitate zirconium and hafnium hydroxides, which are not soluble in excess of the reagent. Ammonium oxalate or oxalic acid precipitate the oxalates, soluble in excess of the reagents. Separation from iron may be accomplished through the slight solubility of the potassium complex fluorides.

Hafnium and zirconium are extremely difficult to separate from each other. The greatest difference in the solubilities of their compounds appears to exist in the citrates, the hafnium salt being the more soluble. Separation may also be carried out through the fractional precipitation of the phosphates, oxychlorides, and the ammonium and potassium complex fluorides. The per cent of hafnia and zirconia in a sample may be estimated by determination of the density of the oxide mixture. The values for the pure oxides are ZrO_2, 5.73, and HfO_2, 9.68.

Thorium is readily extracted from its ores by digestion with hydrochloric or sulfuric acids. Ammonia and the alkalies precipitate the hydroxide, which is not soluble in excess of the reagent. Thorium and cerium are separated from the rare earths through the very slight solubilities of the iodates, $Th(IO_3)_4$ and $Ce(IO_3)_4$, even in rather concentrated acid. Other slightly soluble compounds are: $K_4Th(SO_4)_2 \cdot 2H_2O$, $ThO \cdot CO_3 \cdot 8H_2O$, $K_2ThF_6 \cdot 4H_2O$, $Th(C_2O_4)_2$, $Th_3(PO_4)_4 \cdot 4H_2O$ and $ThFe(CN)_6$.

GERMANIUM, TIN, AND LEAD

15. Occurrence.—The elements of this group constitute but a very small portion of the earth's crust, the estimated percentages being germanium, 10^{-12}, tin, 10^{-5}, and lead 2×10^{-5}. They do, however, occur frequently in workable deposits.

Germanium is found in many sulfide ores, especially those of silver, lead, tin, antimony, and zinc. In a number of ores definite sulfide complexes appear to be present, such as Ag_4GeS_6 and Pb_2GeS_4.

The most important tin mineral is the oxide, SnO_2, called **cassiterite.** Deposits of cassiterite in Cornwall, England, were worked as early as 1000 B.C. by the Phoenicians. The principal sources of the metal at present are mines in the Malay States, Bolivia, and the Dutch East Indias. Tin also occurs as complex sulfides, e.g. $SnCu_2 \cdot FeS_4$, Pb_5Sn_2, Sb_2S_{12}, and Ag_8SnS_6, and as complex oxides, e.g. $CaSnO_4(BO)_2$ and $CaO \cdot SnO_2 \cdot 3SiO_2 \cdot 2H_2O$, but these minerals are of slight importance.

The principal lead ore is the sulfide or **galena,** PbS, and this is generally associated with sulfides of silver, copper, arsenic, antimony, bismuth, and tin. Other common ores are **cerussite,** $PbCO_3$, and **anglesite,** $PbSO_4$, which appear to have been formed by the weathering of sulfide ores. Complex oxides and oxychlorides of the metals of Groups V and VI also occur.

TABLE III

ATOMIC AND PHYSICAL PROPERTIES OF GERMANIUM, TIN, AND LEAD

	Ge	Sn	Pb
Atomic weight	72.60	118.70	207.22
Atomic number	32	50	82
Isotopes	70, 72, 74	116, 117, 118, 119, 120, 122, 124	206, 208
Electrons in various quantum levels,			
1st	2	2	2
2d	8	8	8
3d	18	18	18
4th	4	18	32
5th		4	18
6th			4
Melting point, °C.	958	231.8	327.5
Boiling point, °C.	2700	2260	1620
Density, g./cc.	5.36	W 7.31 G 5.75	11.34
Electrical resistivity, ohm-cm. at 20 °C.	89×10^{-3}	11.4×10^{-6}	21.9×10^{-6}
Size of M^{+4} ion in crystal, cm. $\times 10^8$ (if $Cl^- = 1.81$)	0.53	0.71	0.84

16. Metallic Germanium.—The metal may be prepared by reduction of the dioxide with carbon at red heat, or by the reduction of the oxide or sulfide by heating with potassium cyanide. Germanium is a greyish-white metal, rather hard and brittle. X-ray data for the solid indicate that the atoms are arranged in a modified diamond structure. The metal is not a good electrical conductor.

17. Tin.—Cassiterite is easily reduced to the metal by smelting with carbon in a reverberatory furnace: $SnO_2 + C = Sn + CO_2$. The liquid metal is drawn off from the furnace and cast into molds. The greatest difficulty in the metallurgy is the purification of the ore before smelting. This is carried out by roasting,

to remove sulfur and arsenic, and if tungsten is present, the ore is fused with sodium carbonate and the tungsten extracted with water. The crude metal usually contains some compounds of iron and arsenic, which may be removed by carefully melting the ingots (liquation), as the compounds melt at temperatures somewhat higher than the pure metal. The yearly production of tin is about 130,000 tons.

Tin exists in three solid forms, with definite transitions as summarized in the following scheme:

$$\mathrm{Sn}\alpha \overset{18^\circ}{=} \mathrm{Sn}\beta \overset{161^\circ}{=} \mathrm{Sn}\gamma \overset{232^\circ}{=} \mathrm{Sn\ (liquid)}$$

The β-form is the ordinary white tin. The transition of white tin to α or grey tin is slow at the transition temperature, but at -50° the transformation is complete in a few days if a little of the latter form is present to start the reaction. The transition is accompanied by an increase in volume, and the product is a brittle substance which is readily powdered. The phenomenon was first observed in cold countries in the disintegration of organ pipes and other tin objects, and was called "**tin disease.**" Grey tin is cubic, with the diamond lattice structure, while white tin is tetragonal with a ditetragonal-bipyramidal lattice. Γ-tin belongs to the rhombic system.

White tin is very malleable, and may be rolled into thin sheets called tinfoil, which is used extensively for wrapping. It is very resistant to corrosion, whence its use in tinning iron and copper surfaces. Tin does not, however, give the galvanic protection afforded by zinc (cf. **VII—4**), since tin is not a more powerful reducing agent than iron. Tin forms many useful alloys. (See Table IV and also Copper and Bismuth.)

18. Lead.—The metallurgy of lead is concerned largely with the reduction of the sulfide, and this may be brought about in several ways. (1) Part of the sulfide may be roasted to the oxide, PbO, or sulfate, $PbSO_4$, and the oxidized ore heated with more of the sulfide: $2PbO + PbS = 3Pb + SO_2$; and $PbSO_4 + PbS = 2Pb + 2SO_2$. (2) The ore may be roasted to the oxide and this reduced with carbon or carbon monoxide: $PbO + CO = Pb + CO_2$. (3) The sulfide may be reduced by heating with scrap iron: $PbS + Fe = Pb + FeS$. The iron may be added as such, or it may be produced in the furnace from a

mixture of iron oxides and carbon. In the United States, the ore is generally first concentrated by "flotation" (cf. **VII—5**) and the smelting process is a mixture of the three methods outlined above. A mixture of part roasted and part unroasted ore with iron oxide and carbon is heated in a blast furnace. Copper present collects in the iron sulfide matte, while silver and gold dissolve in the molten lead. In the refinement of the crude blast furnace lead, the more electropositive impurities are generally removed by melting the metal and keeping it molten for several hours with frequent stirring. The impurities, when oxidized, rise to the surface and are skimmed off. Some lead, especially if high in bismuth, is now refined electrolytically, using as an electrolyte a solution of lead fluosilicate. The crude lead serves as the anode, and a bag about the anode collects the "mud" from which bismuth and the noble metals are recovered. The annual production of lead is about 1,250,000 tons, of which almost half is produced in the United States.

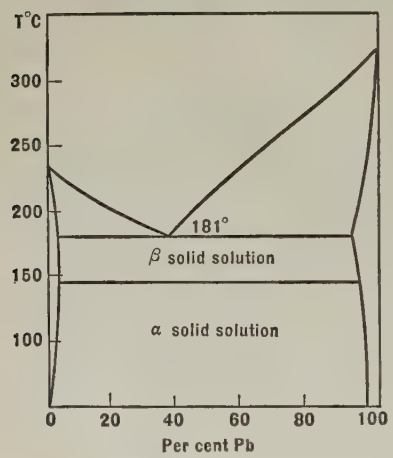


FIG. 1.—Lead-tin temperature-composition curves.

Ordinary lead is a mixture of the two isotopes, 208 and 206. Lead extracted from uranium ores is largely the lower isotope, and has a density of 11.27 as compared with 11.34 for ordinary lead. The crystal lattice of the metal is of the face centered type. The metal is so soft that it can be squirted, under pressure, into pipes and even into fine wire or rolled into thin sheets, but it lacks tensile strength. Lead may be hardened by the addition of antimony or the alkaline earth metals. The most important industrial uses of lead are in the manufacture of storage batteries, preparation of white lead and other pigments, manufacture of cable coverings, in plumbing, and in acid works. Important alloys of lead are listed in Table IV.

TABLE IV

ALLOYS OF TIN AND LEAD

Britannia	Sn 90, Sb 10	Hard metal, Pb 90, Sb 10
Babbitt	Sn 90, Sb 7, Cu 3	Frary metal, Pb 90, Ca 10
Antifriction	Sn 75, Sb 12.5, Cu 17.5	Type metal, Pb 82, Sb 15, Sn 3
Solder	Sn 50, Pb 50	White metal, Pb 75, Sn 19, Cu 1
Pewter	Sn 80 Pb 20	Rose metal, Bi 50, Pb 27.1, Sn 22.9

19. Reactions of the Metals.—The metals are powerful reducing agents in the presence of an alkaline solution and fairly strong in acid solutions. Pure tin and lead do not evolve hydrogen readily with acids due to high over-voltage effects (Append. I). Lead is quite resistant to the action of even moderately concentrated sulfuric acid, but is readily oxidized by oxygen in the presence of various weak organic acids, e.g. acetic acid.

TABLE V

REACTIONS OF Ge, Sn, AND Pb

$M + O_2 = MO_2$	Lead forms PbO or Pb_3O_4
$M + 2H^+ = M^{++} + H_2$	Not with Ge. Slowly with Sn and Pb
$M + 2S = MS_2$	Lead forms only PbS
$M + 2X_2 = MX_4$	With halogens, except PbI_4
$M + 2OH^- = MO_2^{--} + H_2$	Slowly with Sn and Pb. Ge forms GeO_3^{--}
$M + 2H_2O = MO_2 + 4H^+ + 4E^-$	Ge *ca.* − 0.1, Sn 0.0, Pb − 0.66 (values in volts)
$3Ge + 4HNO_3 = 3GeO_2 + 4NO + 2H_2O$	
$3Sn + 4HNO_3 = 3SnO_2 \cdot H_2O + 4NO + H_2O$	Forms slightly soluble metastannic acid
$3Pb + 8HNO_3 = 3Pb(NO_3)_2 + 2NO + 4H_2O$	
$Pb + 2CH_3CO_2H + \frac{1}{2}O_2 = Pb(CH_3CO_2)_2 + H_2O$	Also with other acids
$Pb + 2H_2O + O_2 = Pb(OH)_2 + H_2O_2$	Slowly at moderate temperatures

GERMANIUM COMPOUNDS

20. Germanium dioxide, GeO_2, is readily formed by roasting the sulfide minerals. The oxide is not soluble in nitric or sulfuric acids, but is dissolved when heated with concentrated hydrofluoric or hydrochloric acids with the formation of volatile **tetrahalides.** The halides are hydrolyzed in water with the precipitation of the hydrated dioxide, except the fluoride, which forms a mixture of the dioxide and **fluogermanic** acid, H_2GeF_6.

The potassium salt, K_2GeF_6, is but slightly soluble. The dioxide is soluble in alkalies forming **germanates,** e.g. Na_2GeO_3.

Germanium **disulfide,** GeS_2, may be precipitated in strong sulfuric acid by hydrogen sulfide, but yields a colloidal suspension in dilute acid. It is soluble in alkali sulfide, forming **thiogermanates.**

Germanium resembles silicon in the formation of an unstable **hydride,** GeH_4, and also traces of the heavier compounds, Ge_2H_6 and Ge_3H_8, when germanium compounds are reduced with aluminum in alkaline solution. The metal heated in a stream of hydrogen chloride forms **germanium chloroform,** $GeHCl_3$. This compound hydrolyzes to form **germanous acid,** which appears to resemble formic acid in structure: $GeHCl_3 + 2H_2O = 3HCl + HGeO(OH)$. The acid is soluble in alkalies, forming **germanites,** and upon heating forms **germanous oxide,** GeO, which possesses basic properties in that it is soluble in acids. **Germanous halides** and the **sulfides** may be prepared by heating the tetravalent compounds, e.g. $GeI_4 = GeI_2 + I_2$. The divalent compounds are readily oxidized.

Compounds of Tin

21. Valence States.—The stability of the two valence states of tin in respect to oxidizing and reducing agents is indicated by the following potentials:

	Volts
$Sn = Sn^{++} + 2E^-$	+ 0.13
$Sn = Sn^{++++} + 4E^-$	0.0
$Sn^{++} = Sn^{++++} + 2E$	− 0.13

It follows from these values that the equilibrium, $Sn + Sn^{++++} = 2Sn^{++}$, favors the reaction as written, that is, soluble stannic compounds may be reduced to stannous by the metal. The equilibrium is reversed in hot alkaline solutions: $2SnO_2^{--} + H_2O = Sn + SnO_3^{--} + 2OH^-$.

22. Oxides and Hydroxides.—The **dioxide,** SnO_2, is the principal tin ore. The crystal lattice is similar to rutile. When fused with alkalies, the oxide forms **stannates,** e.g. Na_2SnO_3. The alkali stannates are soluble in water, and upon the addition of acid to the solution precipitate **stannic acid,** H_2SnO_3. This acid or hydroxide is amphoteric, and readily dissolves in excess of either base or acid.

Another acid, or hydrated oxide, **β stannic acid** (also called metastannic acid) is formed by the action of nitric acid upon tin. This compound is not soluble in excess of any acid, but reacts with hydrochloric acid to form a substance not soluble in excess of the acid but soluble in water. The composition of the two acids appears to be the same, the different behavior being due to differences in physical state. Sodium hydroxide dissolves the meta acid, and the salt, $Na_2Sn_5O_{11}4H_2O$, may be crystallized from the solution.

23. Stannous oxide, SnO, may be prepared by heating stannous hydroxide or oxalate, or by heating the metal in a limited supply of oxygen. It burns when heated in air to form the dioxide. **Stannous hydroxide,** $Sn(OH)_2$, is precipitated by the addition of alkalies to stannous solutions. It is also amphoteric, dissolving in alkali hydroxides, but not in ammonia or soluble carbonates. Solutions of **stannites** are powerful reducing agents.

24. Peroxystannic acids, $H_2Sn_2O_7$ and $HSnO_4$, and their salts, are formed by the action of peroxides on stannic solutions, or by the anodic oxidation of cold solutions of alkali stannates.

25. Halides.—The anhydrous **stannic halides** may be prepared by the action of the halogens on the metal and aqueous solutions of the salts by dissolving stannic oxide in the hydrohalic acid. Complex halidostannates are formed in solution and a number of these soluble salts may be obtained upon crystallization, e.g. K_2SnF_6. **Stannic chloride** is important commercially as a mordanting agent. It crystallizes from an acid solution as $SnCl_4 \cdot 5H_2O$ although the anhydrous compound is a liquid. The **ammonium chlorostannate,** $(NH_4)_2SnCl_6$, is also used in dyeing under the name "pink salt."

Stannous halides are readily prepared from the stannic by reduction with tin, or by dissolving the metal in the halogen acid. The solutions are readily oxidized by air. **Stannous chloride** is also important as a mordant. The salt is very soluble in water, but forms the basic salt, Sn(OH)Cl, unless acid is present to prevent hydrolysis.

26. Sulfides.—**Stannous** and **stannic sulfides** may be prepared by fusing the elements together, but the latter is unstable at high temperatures: $SnS_2 = SnS + S$. Hydrogen sulfide percipitates brown stannous and yellow stannic sulfide from dilute acid solutions of stannous and stannic salts respectively. Both sulfides are

soluble in concentrated hydrochloric acid but stannic sulfide, being the more acid in nature, is the less soluble of the two. The disulfide is amphoteric and dissolves in excess of sulfide to form **thiostannates:** $SnS_2 + S^{--} = SnS_3^{--}$. The stannous sulfide is not soluble in excess sulfide unless polysulfide is present, in which case it is oxidized to thiostannate: $SnS + S_2^{--} = SnS_3^{--}$. The thiostannates are not stable in acid solution: $SnS_3^{--} + 2H^+ = H_2SnS_3 = H_2S + SnS_2$.

Stannic sulfide has long been used as a gilding pigment under the name of **mosaic gold.** The preparation is carried out by heating together a mixture of tin, sulfur, ammonium chloride, and mercury. The exact action of the two latter substances is uncertain, but they volatilize and leave the sulfide as brilliant yellow crystals.

27. Other Tin Compounds. Small amounts of the **hydride,** SnH_4, are formed by the cathodic reduction of tin in dilute acid solution. Both stannous and stannic **carbonates** are completely hydrolyzed to the hydroxides. Both of the **nitrates** and the **sulfates** are formed in solution by the action of the acids upon the hydroxides, but they are difficult to crystallize without the formation of basic salts. Slightly soluble **stannous phosphate,** $Sn_5H_2(PO_4)_4 \cdot 3H_2O$, may be precipitated from slightly acid stannous chloride by sodium acid phosphate, and a number of slightly soluble basic and double stannic phosphates are known.

Lead Compounds

28. Valence States.—The most important oxidation reduction potentials for lead and its valence states are given below:

	Volts
$Pb = Pb^{++} + 2E^-$	$+ 0.12$
$Pb + SO_4^{--} = PbSO_4 + 2E^-$	$+ 0.31$
$Pb + 2OH^- = PbO + H_2O + 2E^-$	$+ 0.58$
$Pb^{++} + 2H_2O = PbO_2 + 4H^+ + 2E^-$	$- 1.44$
$PbSO_4 + 2H_2O = PbO_2 + 4H^+ + SO_4^{--} + 2E^-$	$- 1.7$
$PbO + 2OH^- = PbO_2 + H_2O + 2E^-$	$- 0.1$

It follows that lead is a fair reducing agent in acid solutions, and a strong reducing agent in alkaline solutions, and that the dioxide is an extremely powerful oxidizing agent in acid solutions but weak in alkaline solutions.

29. Oxides and Hydroxides.—Lead forms the **monoxide,** PbO,

and the **dioxide,** PbO_2. Two additional oxides appear to be plumbous plumbate salts, the **trioxide,** Pb_2O_3, being $PbPbO_3$, and **red lead,** Pb_3O_4, being Pb_2PbO_4. The existence of a so-called suboxide or its salts is extremely doubtful.

The monoxide, or **litharge,** orange-yellow, is prepared by heating the metal in air; and around 550° C. the other oxides evolve oxygen to form the monoxide. The oxide is soluble in acids and alkalies, forming respectively **plumbous** and **plumbite** ions, and the addition of alkalies and acid, respectively, to these solutions, precipitates the **hydroxide,** $Pb(OH)_2$, which is soluble in excess of either reagent. The hydroxide is a stronger base than stannous hydroxide, as is shown by the formation of a carbonate.

Litharge is used in glazing pottery and in making glass. A mixture with glycerine is sometimes used as a cement, since it sets to a solid lead glyceride.

Red lead or **minium** is made by carefully heating the monoxide at temperatures below 500°. The composition of the product varies with the temperature of roasting, a maximum of PbO_2 (33 per cent) is obtained at about 430°. When treated with nitric acid, it is decomposed: $Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O$. Red lead is used in making flint glass, and as a red pigment. Structural iron is often given a first coat of red lead paint as it serves very effectively to protect the iron from corrosion, due possibly to the iron becoming passive.

30. Lead dioxide may be prepared from red lead as indicated above, but it is most readily formed by the oxidation of lead monoxide or plumbites in dilute alkali solutions, e.g. $PbO + ClO^- = PbO_2 + Cl^-$. The oxide is also readily prepared by the anodic oxidation of solutions of plumbous ion. The dioxide has the rutile type of crystal lattice, and is a fair electrical conductor. It is only slightly soluble in water and is comparatively inert toward hydrogen and hydroxide ions. Concentrated alkalies do, however, dissolve the oxide forming **plumbates,** and soluble metaplumbates may be formed by fusing the oxide with alkalies. Many plumbates, both ortho and meta, of the more basic divalent oxides have also been prepared. The oxide is slowly soluble in dilute nitric acid, but the tetravalent lead ion oxidizes water with the evolution of oxygen. Cold concentrated hydrochloric acid forms liquid tetrachloride, but at ordinary

temperatures chlorine is evolved. For the use of the dioxide in the lead storage battery, see Paragraph 38.

31. Lead Halides.—Lead **tetrafluoride** is formed upon heating the dioxide with potassium acid fluoride, although the product does not appear to be the pure compound. The formation of the **tetrachloride** is discussed in the preceding paragraph. In dilute acid, both halides are hydrolyzed to the dioxide; in the concentrated halogen acids, the **fluoplumbic acid,** H_2PbF_6, and **chloroplumbic acid,** H_2PbCl_6, are formed. Alkali salts of both of these acids have been prepared.

The divalent lead halides are but sparingly soluble in cold water, but the chloride and bromide are readily soluble in hot water, and the iodide partially soluble. The solubility of the halide is decreased in dilute solutions containing the halogen ion but is increased in concentrated solutions, doubtless with the formation of complex ions, such as $PbCl_4^{--}$.

32. Nitrate.—The nitrate, $Pb(NO_3)_2$, is readily soluble, but unless a slight excess of acid is present to prevent hydrolysis, basic nitrates are precipitated.

33. Acetate.—The acetate, $Pb(C_2H_3O_2)\cdot 3H_2O$, called sugar of lead, is one of the few soluble lead salts, and it appears to form a complex ion with excess acetate. Like the nitrate, the solution tends to form basic salts, but the basic compound, $Pb(OH)\text{-}C_2H_3O_2$, is soluble. Both the acetate and nitrate are extremely poisonous.

The dioxide is soluble in glacial acetic acid with the formation of the tetra-acetate, but this compound is completely hydrolyzed in water.

34. Sulfate.—The sulfate, $PbSO_4$, resembles the alkaline earth sulfates in being slightly soluble in water. It is soluble in excess acetate (see above) and in excess alkali it dissolves to form plumbite. The basic sulfate, Pb_2OSO_4, known as the pigment "sublimed white lead," is made by roasting lead sulfide with carbon. The product sublimes and is condensed to a pure white powder. The commercial pigment usually contains excess of $PbSO_4$ and some zinc oxide.

35. Chromate.—The chromate, $PbCrO_4$, is very slightly soluble in water, but dissolves readily in acids with the formation of dichromate, and in bases with the formation of plumbite. It is an important yellow pigment, **chrome-yellow.**

36. Sulfide.—The occurrence of the sulfide in the mineral galena and its metallurgy has been discussed. The sulfide is precipitated from dilute acid solutions by hydrogen sulfide, but is soluble in concentrated hydrochloric acid and in hot $2N$ nitric acid. It is not soluble in excess sulfide. The crystal has the sodium chloride type of lattice. It acts as a rectifier for oscillating electric currents.

37. Lead Carbonate.—Normal lead carbonate, $PbCO_3$, may be prepared by the action of sodium bicarbonate solution upon lead chloride or sulfate. When soluble carbonates are added to a solution of lead ion, the **basic carbonate,** $Pb_3(OH)_2(CO_3)_2$, is formed. This compound is extremely important as the pigment **white lead.** It is prepared commercially by the action of air, carbon dioxide, and acetic acid upon the metal. A small amount of acetic acid serves to convert a large quantity of lead into the carbonate. The following reactions may represent the mechanism of the process: $2Pb + O_2 + 2HAc = 2Pb(OH)Ac$; $6Pb(OH)Ac + 2CO_2 = Pb_3(OH)_2(CO_3)_2 + 3PbAc_2 + 2H_2O$; and $2Pb + O_2 + 2PbAc_2 + 2H_2O = 4Pb(OH)Ac$. In the older forms of the process, perforated lead disks were placed over pots containing acetic acid. Tiers of these pots were stocked with tan bark which decomposed under bacterial action, liberating carbon dioxide and also providing heat. This process required about three months for completion and more rapid methods are now being used to some extent, as for example, the churning of lead dust with acetic acid, air, and carbon dioxide.

The covering power of white lead is excellent but it has the disadvantage of darkening due to the formation of the sulfide, and its poisonous nature is also objectional.

38. Other Lead Compounds.—Lead **orthophosphate,** $Pb_3(PO_4)_2$, may be precipitated from dilute acid plumbous solutions by disodium phosphate. Many basic and double phosphates are also known. Lead **silicate,** $PbSiO_3$, is formed by fusing lead monoxide and silica. It is a constituent of lead glass and of certain glazes used on earthenware.

39. Lead Storage Battery.—The ordinary lead accumulator depends upon the reversibility of the reaction: $Pb + PbO_2 + 4H^+ + 2SO_4^{--} = 2PbSO_4 + 2H_2O$. When fully charged, one electrode consists of a plate of spongy lead, the other electrode a plate impregnated with lead dioxide, and the electrolyte is sulfuric acid. The half reactions for discharge are: $Pb + SO_4^{--}$

$= PbSO_4 + 2E^-$ and $PbO_2 + 4H^+ + SO_4^{--} + 2E^- = PbSO_4 + 2H_2O$. Lead sulfate thus forms on each plate upon discharge, and the concentration of sulfuric acid decreases. The density of the acid under normal conditions is 1.20 at 2.05 volts (charged) and 1.05 at 1.91 volts (discharged). The cell is not completely reversible as is evident from the higher voltage required to reverse the reaction and recharge the cell (Fig. 2). The final rapid increase in the charging voltage curve occurs when all the solid sulfate is used up and the concentration of the lead ion diminishes.

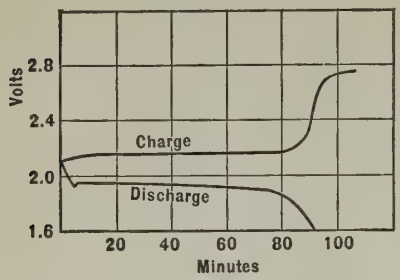


FIG. 2.—Charge and discharge curves for the lead storage battery at 15° C.

40. Analytical.—Advantage is taken of the slight solubility of the sulfides of the group in qualitative analysis. The reactions of these compounds with acids and bases have been discussed, and reference should be made to Appendix VI for the treatment of tin and lead in the systematic separation of the positive ions. The reduction of mercuric chloride, first to mercurous and then to grey metallic mercury by stannous ion, is used as a confirmatory test for tin, and the slight solubilities of $PbSO_4$ and $PbCrO_4$ are used in the confirmation of lead.

Germanium is determined quantitatively by precipitating as the disulfide and weighing as the dioxide.

Tin is sometimes determined gravimetrically as the dioxide, but it is most readily determined by the volumetric titration of stannous ion by iodine: $Sn^{++} + I_2 = Sn^{++++} + 2I^-$. The reduction of any stannic salts prior to the titration is accomplished with aluminum foil in acid solution.

In gravimetric analyses, lead is often precipitated and weighed as the sulfate, $PbSO_4$, chromate, $PbCrO_4$, or molybdate, $PbMoO_4$. In the precipitation as the sulfate, separation from barium is secured by dissolving out the lead in ammonium acetate and dilute sulfuric acid, and reprecipitating. The molybdate method has the advantage that the barium salt is soluble.

Lead is often determined electrolytically by anodic precipitation as the dioxide from a nitric acid solution, using a large platinum anode.

CHAPTER XVI

SUBGROUP V. VANADIUM, COLUMBIUM, TANTALUM

1. The elements of Subgroup V occur in transition series resulting from the building up of the number of electrons in the outer shell of the kernel from eight to eighteen (Append. XVIII); and there is some uncertainty as to the location of the five valence electrons. Spectral data indicate that the normal gaseous atoms have two electrons in the outer level, so that three additional valence electrons must, in the normal atom, be located in the lower level. However, all five valence electrons are removable, and all members of the group form compounds with + 5 valence numbers.

The elements are semi-noble, steel-like metals with high melting points. Vanadium forms compounds of all its possible positive valences, except + 1. Unlike the main Group V, the + 5 valence becomes more stable with increasing atomic weight; and the pentoxide, which is amphoteric in the case of vanadium, becomes more inert to the action of both acids and bases.

2. Occurrence.—Vanadium is estimated as present in igneous rocks to the extent of 0.025 per cent, and columbium and tantalum are still less abundant.

The principal vanadium minerals are **vanadinite,** $Pb_5(VO_4)Cl$ (analogous to apatite); dechenite, $[Pb, Zn](VO_3)_2$; pucherite, $BiVO_4$; volborthite, $[Cu, Ca]_3(VO_4)_2H_2O$; and roscoelite, a vanadium mica containing V_2O_3. **Carnotite,** $K(UO_2)VO_4 \cdot 3/2H_2O$, is also important as a source of uranium.

Columbium and tantalum usually occur together, the principal minerals are columbite, $FeCb_2O_6$, and tantalite, $FeTa_2O_6$. Other minerals are: pyrochlor, calcium columbate, containing titanium, thorium and rare earths; yttrotantalite and fugersonite, complex oxide mixtures containing largely Ta_2O_5, Cb_2O_5, Yt_2O_3 and Er_2O_3.

3. Metallurgy.—**Vanadium** is extracted from its ores by leaching out the ore with strong hydrochloric acid, and is precipitated from this solution as ammonium vanadate by evaporation of the solution with excess of ammonium chloride. Ammonium vanadate, when roasted, yields the oxide.

The preparation of the pure metal is a difficult operation. The reduction of the pentoxide with carbon in an electric furnace yields mostly carbide; and the reduction with aluminum gives a mixture of the metal and dioxide. The reduction of the dichloride with hydrogen is a satisfactory method of preparing the metal on a small scale. Very little of the pure metal is prepared commercially, however, as the steel industry, which is the principal consumer, employs ferrovanadium. This is manufactured by the reduction of the mixed oxides with carbon in an electric furnace.

The separation of pure **columbium** and **tantalum** oxides from their ores is largely an analytical problem (Par. **17**). The metals may be prepared by the reduction of the complex alkali fluorides with sodium, or the oxide with metallic cerium. At the temperature of the electric furnace, the oxides may be decomposed to the metals by heating in a vacuum. Reduction of the oxides with hydrogen is also employed.

TABLE I

Atomic and Physical Properties

	V	Cb	Ta
Atomic weight	50.96	93.1	181.5
Atomic numbers	23	41	73
Electrons in various quantum levels,			
1st	2	2	2
2d	8	8	8
3d	11 (8 + 3)	18	18
4th	2	11 (8 + 3)	32
5th		2	11 (8 + 3)
6th			2
Melting point, °C	1710	1950	2770
Boiling point, °C	3000 (?)	3300	4100 (?)
Density	5.9	8.4	16.6
Electrical resistivity, ohms-cm. at 25 °C			15×10^{-6}
Ionization potential of gaseous atom, volts	6.3		
Tensile strength, lb. sq. in.			130,000
Radius of metal ions M^{+5} in crystals, cm. $\times 10^8$ (if $Cl^- = 1.81$)	0.59	0.70	

4. The Metals.—The more important physical properties are given in Table I. The metals are grey or silver white in color,

and do not tarnish readily. Though very hard, they may be rolled or hammered, and drawn into wire. Vanadium is used extensively in the steel industry (cf. **XIX—7**), to add tensile strength to steel. Columbium has no commercial uses at present. Tantalum was formerly employed in electric light filaments, but has been replaced by tungsten. The metal is extremely resistant to chemical action at ordinary temperatures and is being employed in many chemical manufacturing processes, displacing platinum, and other expensive metals. Due to the passive nature of tantalum, it exhibits, to a high degree, an electrolytic valve action (see Aluminum, **VI—17**) and is employed in cells to act as current rectifiers. Tantalum absorbs gases readily at high temperatures; and becomes hard and brittle. For this reason, the metal must be worked cold or in a vacuum.

5. Reactions of the Metals.—The metals are attacked by oxygen only when heated. Vanadium is dissolved by nitric acid and other powerful oxidizing agents (Par. **6**); but columbium and tantalum are attacked readily only by a mixture of nitric and hydrofluoric acids. The general reactions of the group are summarized in Table II.

TABLE II

REACTIONS OF VANADIUM, COLUMBIUM, AND TANTALUM

$4M + 5O_2 = 2M_2O_5$	Heated. V also forms VO_2
$2M + 5X_2 = 2MX_5$	Heated. Ta and Cb with F, Cl, and Br. V forms only VCl_4 and VBr_3.
$6M + 5N_2 = 2M_3N_5$	Heated. V forms VN
$M + C = MC$	High temperature
$M + 2S = MS_2$	Heated. V forms V_2S_5 also
$M + 5NaOH = NaMO_3 + 5/2H_2 + 2Na_2O$	Fused. Ta and Cb form $Na_8M_6O_{19}$
$3M + 15HF + 5HNO_3 = 3H_2MOF_5 + 5NO + 7H_2O$	Also other complex fluo-acids
$2V + Si = V_2Si$	High temperature
$2Cb + H_2 = 2CbH$	

VANADIUM COMPOUNDS

6. Valence States.—Vanadium forms compounds possessing the positive valence numbers 2, 3, 4, and 5. The two lower valences are basic; but the two higher are amphoteric, though in the aqueous solutions, the positive ions exist only as vanadyl, VO^{++}, and pervanadyl, VO^{+++}, or vanadol, VO_2^+.

Oxidation-reduction potentials involving the various valences are summarized below:

	Volts
$V^{++} = V^{+++} + E^-$	+ 0.2
$V^{+++} + H_2O = VO^{++} + 2H^+ + E^-$	− 0.4
$VO^{++} + 2H_2O = HVO_3 + 3H^+ + E^-$	− 1.1
$V + H_2O = VO^{++} + 2H^+ + 4E^-$	− 0.3
$V + 4OH^- = VO_2 + 2H_2O + 4E^-$	+ 0.45

From these values, it follows that vanadic acid in concentrated hydrogen ion is an extremely powerful oxidizing agent; but the hydrogen ion is involved to such a high power that the potential decreases markedly in dilute acid, so that vanadate in neutral solution is not easily reduced to the dioxide. In normal acid, vanadic acid is reduced by vanadic ion: $HVO_3 + V^{+++} + H^+ = 2VO^{++} + H_2O$; but the reaction appears to be reversed in neutral solution. Vanadous ion, V^{++}, is a strong reducing agent, and vanadic ion is fairly strong. The metal is oxidized by moderate oxidizing agents in acid solution to the tetravalent state and by powerful agents to vanadate.

7. Divalent Vanadium.—The monoxide, VO, is prepared by the reduction of vanadyl chloride, $VOCl_2$, by carbon, zinc, or hydrogen at red heat. The oxide is semi-metallic in appearance and was considered by Berzelius to be the metal. The **hydroxide,** $V(OH)_2$, is but slightly soluble. Its salts in solution have a deep violet color. The **sulfate,** VSO_4, is prepared in solution by the reduction of sulfuric acid solutions of vanadates by zinc, or by cathodic reduction in an atmosphere of carbon dioxide. The solid hydrate, $VSO_4 \cdot 7H_2O$, may be obtained upon evaporation, and **double sulfates** are formed with the alkali sulfates, $M_2V(SO_4)_26H_2O$. The sulfate solution absorbs nitric oxide, similar to ferrous ion, and the **complex cyanide,** $V(CN)_6^{----}$, is similar to ferrocyanide in the solubilities of its salts. The anhydrous **chloride** and the **sulfide** are prepared, respectively, by the reactions: $VCl_4 + H_2 = VCl_2 + 2HCl$, and $V_2S_3 + H_2 = 2VS + H_2S$. The latter is not soluble in dilute hydrogen ion or in sulfide ion.

8. Trivalent Vanadium.—In formulas and solubilities, the vanadic compounds resemble ferric, but unlike the latter, they are readily oxidized. The salts in solution are green; and the green **hydroxide,** $V(OH)_3$, is precipitated from solutions of its salts by ammonia or alkali hydroxides. The **sesquioxide,** V_2O_3, may be obtained by reducing the pentoxide with hydrogen or

carbon, and the product is insoluble in most acids. Solutions of the **halides** may be prepared by dissolving the hydroxide in the halogen acid. The anhydrous compounds may be prepared by reactions analogous to the following: $2VCl_4 = 2VCl_3 + Cl_2$, and $V_2O_3 + 3Br_2 + C = 2VBr_3 + 3CO$. The **oxychloride, VOCl,** is but slightly soluble. Reduction of sulfuric acid solutions of the pentoxide gives **vanadic sulfate,** $V_2(SO_4)_3$, in solution; this salt readily forms alums. The oxide reacts when heated with ammonia, and with hydrogen sulfide, to give the **nitride,** VN, and the **sulfide,** V_2O_3, respectively. The latter is soluble in dilute acids.

Vanadic ion forms many complex and double salts, the most important being **double fluorides,** as $(NH_4)_3VF_6$, or $(NH_4)_2VF_5$; **double oxalates** as, $K_3V(C_2O_4)_3 \cdot 3H_2O$; complex cyanides as $K_3V(CN)_6$; and sulfocyanides, $K_3V(CNS)_6$.

9. Tetravalent Vanadium.—The **dioxide,** VO_2, may be obtained by partial reduction of the pentoxide; the **hydrated oxide,** $2VO_2 \cdot 7H_2O$, is precipitated by the addition of sodium carbonate to vanadyl salts in solution. The oxide is stable in air. It is soluble in the alkali hydroxide and in ammonia, forming **vanadites,** e.g. $K_2V_4O_9 \cdot 7H_2O$. These compounds in solution have a deep black color, are not readily oxidized, and form slightly soluble vanadites with the heavy metals.

The reduction of acid solutions of the pentoxide with mild reducing agents, as sulfur dioxide or hydrogen sulfide, yields blue solutions of **vanadyl salts,** containing the ion, VO^{++}. Similar solutions are formed by dissolving the dioxide in acids, e.g. $VOCl_2$, $VOBr_2$, and $VOSO_4$. The **anhydrous chloride** is formed by the reactions: $V + 2Cl_2 = VCl_4$, and $VOCl_3 + 1/2Cl_2 + C = VCl_4 + CO$. It is a heavy liquid with an extremely low melting point. The water solutions hydrolyze to vanadyl chloride. The addition of sulfide to an acid vanadyl solution precipitates the **sulfide,** VS_2, which is soluble in excess sulfide to form **thiovanadites.**

10. Pentavalent Vanadium.—The **oxide,** V_2O_5, may be prepared by roasting ammonium metavanadate, NH_4VO_3; or by the hydrolysis of pervanadyl chloride, $VOCl_3$. It is somewhat soluble in water to give a slightly acid solution. **Metavanadic acid,** HVO_3, may be precipitated as golden yellow solid by the action of sulfurous acid upon copper vanadate. The acid is

sometimes employed as gold bronze. **Pyrovanadic acid,** $H_4V_2O_7$, is precipitated by the addition of nitric acid to vanadate solutions.

Sodium salts of the **meta-, ortho-, pyro-,** and **hexa-vanadic** acids are known: $NaVO_3$, Na_3VO_4, $Na_4V_2O_7$, $Na_2H_2V_6O_{17}$. The metavanadates of sodium, potassium, ammonium, barium, and lead are but slightly soluble in cold water; but salts of other positive ions are soluble, and the color is generally yellow. The alkali pyrovanadates are soluble. In solution ortho-vanadate is readily hydrolyzed: $2VO_4^{---} + H_2O = V_2O_7^{----} + 2OH^-$. At high temperatures, the ortho salts are stable, however, and constitute many of the vanadium minerals. The most important compound is probably ammonium metavanadate, NH_4VO_3, which is precipitated by excess ammonium chloride from meta- and hypo-vanadate solutions.

The alkali metavanadates are readily converted to **peroxy-vanadates,** MVO_4, by hydrogen peroxide; and peroxyvanadic acid, HVO_4, is formed when the pentoxide is added to a solution of hydrogen peroxide in sulfuric acid. The solution has a deep red color.

The pentoxide is soluble in concentrated hydrofluoric and sulfuric acids with the formation of pervanadyl compounds in solution, e.g. **pervanadyl fluoride,** VOF_3, **pervanadyl sulfate,** $(VO)_2(SO_4)_3$. The latter may be obtained as a red-brown solid upon evaporating the acid solution, and basic salts as, $VO(OH)$-SO_4, are also formed. With concentrated hydrochloric acid, chlorine is evolved and the dioxide formed. However, the **pervanadyl chloride** may be made by the action of chlorine upon VO or V_2O_3, or upon a heated mixture of the pentoxide and carbon. The chloride is a heavy low melting liquid with a lemon-yellow color. It fumes in moist air and is hydrolyzed by water to vanadic acid. **Complex oxyfluovanadates,** as K_2VOF_5 and $K_2VO_2F_3$, are precipitated by the addition of potassium fluoride to the pervanadyl fluoride solutions.

Ammonium sulfide acts upon vanadate solutions to form **thiovanadate,** VS_4^{---}. The addition of acid to this solution precipitates the **sulfide,** V_2S_5, or possibly a mixture of V_2S_5 and VS_2.

Columbium Compounds

11. Valence States.—The compounds of lower valence are much less stable than in the case of vanadium. The only

pentavalent compounds which may be obtained in acid solution are the complex fluoride and chloride, and these solutions may be reduced quantitatively by zinc in the cold to a blue solution of trivalent columbium; but, if the solution is heated, a precipitate of mixed oxides, possibly CbO_2 and Cb_2O_3, is formed. The trivalent compounds in solution are oxidized very rapidly by oxygen. The oxychloride, $CbOF_3$, may be reduced by sodium to the monoxide, CbO, which dissolves in acid with the liberation of hydrogen. The pentoxide may be reduced by magnesium to the dioxide, CbO_2, which is not attacked by acids, but burns in air when heated.

Due to the passivity of the metal and the inertness of the oxide, very little is known about the true oxidation-reduction potentials of columbium, and the following values are only approximations:

	Volts
$2Cb + 5H_2O = Cb_2O_5 + 10H^+ + 10E^-$	0.0(?)
$2Cb^{+++} + 5H_2O = Cb_2O_5 + 10H^+ + 4E^-$	0.1(?)

12. Pentoxide and Columbates.—The pentoxide, Cb_2O_5, may be prepared by decomposing the potassium oxyfluoride with sulfuric acid. The pentachloride hydrolyzes in water to give the **meta-acid,** $HCbO_3$. The oxide and acid when fused with alkalies or alkali carbonates yield complex columbates. **Potassium hexacolumbate,** $K_8Cb_6O_{19}\cdot 16H_2O$, is readily soluble in water, and with excess of alkali forms a number of other salts, such as $K_4Cb_2O_7\cdot 11H_2O$.

Peroxycolumbates are formed by the action of peroxides upon columbates; and the **peroxyacid,** $HCbO_4$, is obtained as a yellow solid when columbic acid is warmed with hydrogen peroxide.

Halogen Compounds.—Columbic acid is soluble in hydrofluoric acid; the addition of potassium fluoride to the solution yields **fluocolumbite,** K_2CbF_7, and in less concentrated acid double salts of the oxyfluoride, such as K_2CbOF_5.

The **pentachloride,** $CbCl_5$, is formed by passing chlorine over a heated mixture of the oxide and carbon; or sulfur chloride, S_2Cl_2, over the oxide. The pentachloride is soluble in hydrochloric acid. The **oxychloride** is a volatile solid, and like the chloride, is completely hydrolyzed in water. Corresponding compounds of fluorine and bromine have also been prepared, which have rather similar properties.

At red heat, the pentachloride decomposes into the **trichloride,** $CbCl_3$. This anhydrous chloride is not decomposed by water, but is readily oxidized with nitric acid, and when heated reacts with carbon dioxide: $CbCl_3 + CO_2 = CbOCl_3 + CO$.

Other Compounds.—The metal heated in nitrogen at 1200° forms the **nitride,** Cb_3N_5. Mixed oxide-nitride compounds result from the action of ammonia upon the oxide at red heat.

The metal unites with hydrogen when heated to form the **hydride,** CbH, which is not attacked by acids, but readily burns in air.

The oxide is not converted into sulfide by ammonium sulfide, but an **oxysulfide,** $CbOS_3$, forms when the oxide is heated in an atmosphere of carbon dioxide and carbon disulfide.

Tantalum Compounds

13. Although there is very little experimental work on the oxidation-reduction potentials of tantalum, the value for the heat of formation of the pentoxide, 301,500 cal., leads to the following approximate potentials:

	Volts
$2Ta + 5H_2O = Ta_2O_5 + 10H^+ + 10E^-$	-0.2
$2Ta + 10\,OH^- = Ta_2O_5 + 5H_2O + 10E^-$	$+0.7$

These values correspond to the fact that the metal is much more difficult to oxidize by acid oxidizing agents than by alkaline. However, the reduction of the pentoxide to the metal is extremely difficult, apparently due to the slowness of the reaction.

No lower valence compounds are stable in aqueous solution. The divalent chloride has been prepared at high temperatures, but the water solution evolves hydrogen rapidly.

14. Pentoxide and Tantalates.—The pentoxide, Ta_2O_5, is formed when the metal burns in air. It is left as a residue when tantalates are fused with potassium acid sulfate, and the product extracted with hydrochloric acid. The oxide is very inert, but when fused with alkali hydroxides forms **hexatantalates,** e.g. $Na_8Ta_6O_{19}\cdot 25H_2O$. These compounds are soluble in water. When ignited with ammonium chloride, **metatanlates,** e.g. $NaTaO_3$, are formed; these are not soluble. The **meta-acid,** $HTaO_3$, is precipitated when the pentachloride is added to water.

A solution of potassium hexatantalate gives with peroxide a

peroxytantalate, $K_3TaO_8 \cdot 1/2H_2O$, which may be precipitated from the solution by the addition of alcohol. The compound is decomposed by sulfuric acid to give the acid, $HTaO_4$, which is fairly stable.

The pentoxide reduced with magnesium yields a **monoxide,** TaO, which is not soluble in acids, and burns in air to the pentoxide.

The ignited pentoxide is not soluble in any acid, but the hydrated oxide dissolves in hydrofluoric acid, and either dissolves slightly, or is peptized by other acids.

15. Compounds with the Halogens.—The **pentafluoride, chloride,** and **bromide,** form when the metal is heated in the corresponding halogen. Alkali **fluotantalates,** e.g. K_2TaF_7, are obtained by dissolving the hydrated pentoxide in hydrofluoric acid, and adding alkali fluoride. These compounds are easily soluble in hot water, but much less soluble in cold. When the solution of the potassium salts is boiled, an **oxyfluoride,** $K_4Ta_4O_5F_{14}$, precipitates.

The pentachloride and bromide are most readily prepared by heating a mixture of the oxide and carbon in a stream of chlorine. These compounds are readily volatile around 150°, and are completely hydrolyzed by water.

16. Other Compounds.—The **sulfide,** TaS_2, is said to be formed by the action of hydrogen and carbon disulfide upon the heated oxide. It is not soluble in hydrogen ion. When the chloride is heated in ammonia at not too high a temperature, a bright red **nitride,** Ta_3N_5, is formed. At higher temperatures, the compound TaN is produced. The pentanitride is also formed when the metal is heated in nitrogen at 1000° C.

The **carbide,** TaC, forms when the oxide is reduced with carbon at high temperatures.

17. Analytical.—The slight solubility of the oxides of vanadium, columbium, and tantalum in dilute hydrogen ion, and in oxidizing agents, and their ready solubility in hydrofluoric acid, places them analytically in a group consisting of Sb_2O_5, SnO_2, WO_3, MoO_3, TeO_2, V_2O_4, TiO_2, Ta_2O_5, Cb_2O_5, and Bi_2O_3, together with phosphates of Sn, Ti, and Zr. When these oxides are dissolved in hydrofluoric acid and treated with ammonium sulfide, a separation is obtained, giving in the filtrate, the thiosalts of Sb, Sn, W, Mo, Te, V, and a residue of TiO_2, Ta_2O_5, Cb_2O_5,

Bi_2O_3, and Ti and Zr phosphate or vanadate. The presence of vanadium in the thio-salt solution is recognized by the violet red color of $(NH_4)_3VS_4$.

When the TiO_2, Ta_2O_5, etc. residue above is boiled with sodium salicylate solution, the titanium and vanadium are extracted. The residue is fused with K_2CO_3; and $K_8Ta_3O_{18}$ and $K_8Cb_3O_{18}$ are obtained in solution by extracting with cold water. The tantalum is separated from the columbium by the smaller solubility of the potassium oxyfluotantalate, and the columbium recognized by reduction to $CbCl_3$, blue, with zinc, and the reaction of this solution with mercuric chloride to give mercurous chloride.

In gravimetric determinations, these elements are usually separated and weighed as the pentoxides. Vanadium and columbium are determined volumetrically by reduction to vanadyl and to trivalent columbium, and titration with permanganate.

CHAPTER XVII

SUBGROUP VI. CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM

1. The elements of Subgroup VI have as a maximum positive valence number 6, and in this valence show many properties common to each other, as well as to sulfur in the sulfates. In addition, the elements of the group have a variety of lower valences, in which they do not resemble each other as much as they do the elements of higher and lower atomic numbers; especially is this true of chromium, whose lower valences are similar to the corresponding valences of vanadium and manganese. This fact is to be correlated with the position of the elements in transition series in which an eight electron shell is being converted to an eighteen electron shell (Append. XVIII). One of the most striking properties of the hexavalent compounds is the tendency to form poly-acids. This tendency reaches a maximum in molybdenum, which forms acids containing many molecules of the trioxide. The acidic nature of the hexavalent compounds decreases with increasing size of the ions.

The metals have very high melting points, that of tungsten being higher than that of any other metal. They are also very tough, and advantage is taken of this in forming many important alloys with iron. Uranium is highly electropositive, the others slightly so.

Uranium is radioactive; this property is discussed in connection with the other radioactive elements, Chapter **XXI**.

2. Occurrence.—The metals do not occur free in nature. Chromium is the most abundant of the group, and is present to the extent of about 0.05 per cent in igneous rocks, usually as Cr_2O_3, replacing Al_2O_3 in aluminates. The most important chromium ore is **chromite,** $Fe(Cr_2O_4)$, or $FeO \cdot Cr_2O_3$. Lead chromate, $PbCrO_4$, and other chromates of the heavy metals also occur.

3. Molybdenum is most frequently found as the sulfide, **molybdenite,** MoS_2, which resembles graphite in appearance. It also occurs as molybdates, especially $PbMoO_4$ and $Fe_2(MoO_4)_3 \cdot 7.5H_2O$.

The most important tungsten ore is **wolframite,** an isomorphous ferrous-manganous tungstate, [Fe, Mn]WO_4. Other tungstates, as $CaWO_4$, $PbWO_4$, and $CuWO_4$, and the trioxide, WO_3, or wolfram ochre, are also found.

Uranium is found as **pitchblende** or **uraninite,** which is about 80 per cent U_3O_8, together with the rare earth and other oxides; and as **carnotite,** $K(UO_2)VO_4 \cdot 3/2H_2O$ and **autunite** $Ca(UO_2)_2(PO_4)_2 8H_2O$.

Metals and Metallurgy

4. Chromium.—The greater portion of metallic chromium is utilized in chrome steel, and for this use ferrochrome is prepared by the direct reduction of chromite by carbon: $FeCr_2O_4 + 4C = Fe + 2Cr + 4CO$. For the preparation of chromium compounds, the ore is usually fused with sodium carbonate in air: $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 = 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2$; the sodium chromate is then extracted with water. The pure metal is conveniently prepared by reducing chromic oxide with aluminum (Goldschmidt reaction), or with carbon in an electric furnace. The electrolytic deposition of chromium on iron or copper has recently assumed importance. The electrolyte used is an acid chromic chromate solution containing sulfate, phosphate, borate, or other acid radicals.

Chromium is similar to platinum in luster, and this together with its high resistance to corrosion, has resulted in the use of the electroplated metal on motor cars and miscellaneous domestic appliances.

Chrome steel (about 2 per cent Cr) is very hard and tough. **Stainless steel** (14 per cent Cr) is used in the manufacture of cutlery, valves, turbine blades, etc. **Nichrome** (60 per cent Ni, 15 per cent Cr, and 25 per cent Fe) is used as resistance wire in electrical heaters. Chromium, with cobalt and tungsten, or molybdenum, forms an alloy known as **stellite,** suitable for high-speed tools (cf. **XIX—19**).

5. Molybdenum.—The sulfide ore is generally roasted to the trioxide which is then extracted with ammonia. Solid ammonium molybdate is obtained when the solution is evaporated, and this yields the trioxide upon ignition. The metal is prepared by the reduction of the oxide by carbon in an electric furnace, or by the reduction of the oxide or chloride by hydrogen. Molybdenum is silver white in color, tough, and ductile. It is

added to steel as a substitute for nickel or vanadium as a toughener, and is substituted sometimes for tungsten in tool steel.

6. Tungsten.—Tungsten is generally obtained from wolframite ores by fusion with sodium carbonate, to convert to sodium tungstate, which is then extracted with water, and the solution digested with hydrochloric acid to precipitate tungstic acid. The acid is reduced by heating strongly with carbon, but the product is a powder, as the temperature is far below the melting point of the metal. Rods of the metal are formed by sintering the particles together by passing a strong electric current through the compressed powder. The most important use of the pure

TABLE I

Atomic and Physical Properties

	Cr	Mo	W	U
Atomic weight	52.01	96.0	184.0	238.17
Atomic number	24	42	74	92
Isotopes	none	—	—	—
Electrons in various quantum levels, 1st	2	2	2	2
2d	8	8	8	8
3d	8 + 4	18	18	18
4th	2	8 + 4	32	32
5th		2	8 + 4	18
6th			2	8 + 4
7th				2
Density	7.1	10.2	19.3	18.7
Melting point, °C.	1615	2620	3370	1850
Boiling point, °C.	2200	3700	5900	
Tensile strength, lbs. per sq. in.			590,000	
Electrical resistivity, ohm-cm.	2.6×10^{-6}	4.8×10^{-6}	5.5×10^{-6}	6.0×10^{-6}
Ionization potential, volts	6.74	7.35		
Radius of M^{+6} ion in crystals, cm. $\times 10^{8}$ (if $Cl^{-} = 1.81$)	0.52	0.62		

metal is the manufacture of filaments for electric lights, a use which depends largely upon the extremely high melting point of the metal. In order to draw the metal into wire, it is necessary to subject the rod to severe working at a low temperature to break up the large crystals which form when the metal is heated

and render it brittle. The tensile strength of the drawn wire exceeds that of any other metallic substance.

Ferro-tungsten can be prepared by the reduction of the purer forms of iron tungstate ore with carbon. It is employed in the manufacture of tool-steel (see Chromium) and other tungsten steels (see Iron).

7. Uranium.—In the extraction of uranium from pitchblende, the ore is generally roasted with alkali carbonate and some nitrate to convert the oxide, U_3O_8, into alkali uranate. After washing with water the ore is treated with sulfuric acid, which dissolves out the uranium as uranyl sulfate, UO_2SO_4. The metal is prepared by the reduction of the oxides by carbon in an electric furnace. Uranium is a heavy "white" metal with a much lower melting point than tungsten. It is highly electropositive and has no important commercial applications.

TABLE II

Reaction Products of the Elements

Reaction with	Cr	Mo	W	U
O_2	Cr_2O_3	MoO_3	WO_3	UO_3 U_3O_8
F_2	CrF_3	MoF_6	WF_6	UF_4, UF_6
Cl_2	$CrCl_3$	$MoCl_5$	WCl_6	UCl_4, UCl_5
Br_2	$CrBr_3$	$MoBr_4$	WBr_6	UBr_5
I_2	CrI_2	No action at 500°	WI_2	UI_4
H^+	Cr^{++}, Cr^{+++} (slow)	No action	No action	U^{+}_4
OH^-	CrO_2^- (slow)	No action	WO_4^{--}	UO_2
HNO_3	Cr^{+++}	MoO_3	WO_3	UO_2^{++}
C	Cr_2C_3	Mo_2C, MoC	W_2C, WC	U_2C_3
N_2	CrN	No action at 1000°	No action at 2000°, WN_2 at 2500°	U_3N_4
S	CrS	MoS_2, Mo_2S_3	WS_2	US_2
B	CrB, Cr_3B	Mo_3B_4	WB_2	UB_2

8. Reactions of the Metals.—The reactions of the metals with common reagents are so varied in nature as to render them difficult to summarize in the form of general group reactions; however, the principal reaction products have been summarized

in Table II. The lighter members of the group exhibit to a high degree the property of passivity, and their reactions with powerful oxidizing agents are thus often extremely slow.

Compounds of Chromium

9. Valence States.—Chromium forms compounds in which it has the valence numbers + 2 (chromous), + 3 (chromic) and + 6 (chromate). The + 2 valence is basic, the + 3 valence is amphoteric, and the + 6 valence is acidic. The potential relations between the valence states are summarized in the following half reactions:

	Volts
$Cr = Cr^{++} + 2E^-$	+ 0.6
$Cr^{++} = Cr^{+++} + E^-$	+ 0.4
$2Cr^{+++} + 7H_2O = Cr_2O_7^{--} + 14H^+ + 6E^-$	− 1.3
$H_2CrO_3^- + 4OH^- = CrO_4^{--} + 3H_2O + 3E^-$	− 0.2 (?)

It is evident from these values that the chromate in acid solution is a powerful oxidizing agent. The equilibrium, $Cr + 2Cr^{+++} = 3Cr^{++}$, favors the formation of chromous ion, but the latter is such a powerful reducing agent that its solutions are oxidized even by very weak oxidizing agents to chromic ion.

10. Chromous Compounds.—Chromous compounds are somewhat similar to ferrous. **Chromous hydroxide,** $Cr(OH)_2$, is a slightly soluble, brownish yellow substance, which is oxidized readily in air and when heated liberates hydrogen: $2Cr(OH)_2 = Cr_2O_3 + H_2O + H_2$. Solutions of chromous ion are blue, and may be prepared by the reduction of chromic solutions by the metal or by zinc (see above). The **chloride** and **sulfate** are soluble. The former may be prepared as an anhydrous salt, by heating the metal in hydrogen chloride. The **sulfide,** CrS, and **carbonate,** $CrCO_3$, are but slightly soluble, and the **acetate,** $Cr(C_2H_3O_2)_2$, but moderately so.

11. Chromic Compounds.—The **oxide,** Cr_2O_3, is the most stable of the chromium oxides, and is formed by heating the metal or other oxides in air. Due to its fine green color it is used as a pigment, **chrome green.** This is generally prepared by igniting sodium dichromate with sulfur or ammonium chloride: $Na_2Cr_2O_7 + S = Cr_2O_3 + Na_2SO_4$ and $Na_2Cr_2O_7 + 2NH_4Cl = Cr_2O_3 + 2NaCl + N_2 + 4H_2O$. The oxide is isomorphous with corundum, Al_2O_3. **A hydrated oxide,** $Cr_2O_3 \cdot 2H_2O$ is formed by the hydrolysis of chromic salts in boiling water.

In its amphoteric properties **chromic hydroxide,** $Cr(OH)_3$, or $Cr_2O_3 \cdot nH_2O$, resembles aluminum hydroxide, and like the latter is precipitated by ammonium hydroxide, and by solutions of alkali sulfides and carbonates. Excess of alkali hydroxide dissolves the precipitate with the formation of **chromites,** but the hydroxide or hydrated oxide is precipitated upon boiling. Chromites are readily formed by fusing the oxide with metal oxides, and such compounds constitute the common chromium minerals, the most important being **ferrous chromite,** $FeCr_2O_4$. Chromite is used extensively as a refractory, especially in lining open-hearth furnaces used in the manufacture of steel.

12. Chromic ion forms numerous coordination complexes, especially with ammonia, water, halides, cyanide, and thiocyanate. A number of these are tabulated below. The coordination number of chromium is six. In solution these compounds dissociate into the complex ion and the ions placed outside the bracket.

$[Cr(NH_3)_6]Cl_3$	$[Cr(NH_3)_6](CNS)_3$	$[Cr(NH_3)_5(H_2O)]Cl_3$
$[Cr(NH_3)_5Cl]Cl_2$	$[Cr(NH_3)_3(CNS)_3]$	$[Cr(NH_3)_5NO_2]Cl_2$
$[Cr(H_2O)_6]Cl_3$	$[Cr(CNS)_6]K_3$	$[Cr_4O(SO_4)_4]SO_4$
$[Cr(H_2O)_4Cl_2]Cl$	$[Cr(CN)_6]K_3$	$[Cr(OH)(NH_3)_5]Br_2$

The two water-chloride complexes are of especial interest. The complex ion, $[Cr(H_2O)_6]^{+++}$, has a violet color, and is present largely in dilute chromic ion solutions, while the complex, $[Cr(H_2O)_4Cl_2]^+$, is green and forms in more concentrated solutions in presence of excess chloride. The rates of transition are slow, however, and the two ions may be obtained in the same solution. Only one-third of the chloride may be precipitated from the green solution by silver ion.

13. Chromic sulfate, $Cr_2(SO_4)_3 \cdot 18H_2O$, may be precipitated by the addition of alcohol to a solution made by dissolving the oxide in sulfuric acid. This solution is violet, probably $Cr(H_2O)_6^{+++}$, *vide supra*, but upon heating a green sulfate solution is formed, which does not form a precipitate upon the addition of alcohol, and in which only one-third of the sulfate is ionized. Upon standing, the green solution reverts to the blue. Chromic sulfate readily forms **alums,** e.g. $KCr(SO_4)_2 \cdot 12H_2O$.

Chromic phosphate, $CrPO_4 \cdot 6H_2O$, precipitates when sodium hydrogen phosphate is added to a chromic solution. Several

other hydrates are formed by carrying out the precipitation at higher temperatures.

14. Chromic Acid and Derivatives.—**Chromic anhydride,** or chromium trioxide, separates as a mass of scarlet needles when a cold concentrated solution of potassium dichromate is treated with concentrated sulfuric acid. It melts without decomposition, but loses oxygen around 250° to form the oxide, $Cr_2O_3 \cdot CrO_3$, or CrO_2, and at higher temperatures, Cr_2O_3. The trioxide is very soluble in water, forming **chromic** and **dichromic acids,** H_2CrO_4 and $H_2Cr_2O_7$. The former may be crystallized from warm concentrated solutions. A solution of chromic acid, formed by adding sulfuric acid to sodium dichromate, is frequently used in the laboratory as **"cleaning solution."**

Like the other members of the sixth periodic group, chromate forms complexes containing varying amounts of the trioxide; and the potassium salts, K_2CrO_4, $K_2Cr_2O_7$, $K_2Cr_3O_{10}$, and $K_2Cr_4O_{13}$ are known. However, only the first two are important, the chromate existing in alkaline solution, and the dichromate in acid solutions. The equilibrium between the two ions is represented by the equation: $2CrO_4^{--} + 2H^+ = Cr_2O_7^{--} + H_2O$, $K = 1.2 \times 10^{14}$. The mechanism of the equilibrium involves the two equilibria: $HCrO_4^- = CrO_4^{--} + H^+$, $K = 7 \times 10^{-7}$, and $2HCrO_4^- = H_2O + Cr_2O_7^{--}$, $K = 60$.

The **alkali chromates** are prepared from chromite by roasting the ore with the alkali carbonate, or mixtures of limestone and alkali sulfate: $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 = 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2$. The cinder is then crushed and extracted with water to obtain the chromate. **Sodium chromate** crystallizes as $Na_2CrO_4 \cdot 10H_2O$, isomorphous with the sulfate, and changes to the hexa hydrate at 79.5°. **Potassium chromate,** K_2CrO_4, is isomorphous with potassium sulfate.

Sodium dichromate, $Na_2Cr_2O_7 \cdot 2H_2O$, is obtained from the chromate by adding acid and crystallizing from the acid solution. Above 82°, the anhydrous salt separates. **Potassium dichromate** is prepared in a similar way. It is not very soluble in cold water, but readily soluble in hot. **Ammonium dichromate,** $(NH_4)_2Cr_2O_7$, is generally made from chromic acid and ammonia. Upon heating, it decomposes according to the equation: $(NH_4)_2Cr_2O_7 = Cr_2O_3 + N_2 + 4H_2O$.

Dichromates are employed extensively in processes requiring a

strong oxidizing agent. In the chrome-tanning process, the hide is treated with sodium dichromate, which is then reduced, and chromic hydroxide precipitated in the pores of the leather. Dichromate forms with gelatine, when exposed to the light, an insoluble product, and advantage is taken of this fact in a number of photographic processes. Potassium dichromate is important in analytical chemistry in the titration of reducing agents, especially ferrous salts (cf. **XIX—16**).

A number of slightly soluble chromates are important pigments: e.g. **chrome yellow,** $PbCrO_4$; **chrome red,** Pb_2OCrO_4; **zinc chromate** (yellow) $ZnCrO_4$. In general, the solubilities of the chromates are very similar to those of the sulfates.

15. Chromyl Compounds.—**Chromyl chloride,** CrO_2Cl_2, and **fluoride,** CrO_2F_2, may be prepared by distilling dichromate with the alkali halide and sulfuric acid. The chloride is a blood-red liquid, which is hydrolyzed by water to chromic and hydrochloric acids. Intermediate **chlor-chromates** also exist, e.g. $KCrO_3Cl$, and the halides may be replaced from the chromyl compounds with ammonia to form **chromyl diamide,** $CrO_2(NH_2)_2$.

16. Peroxychromates.—Hydrogen peroxide gives with chromate in acid a deep blue solution of peroxychromate. If this solution is shaken with ether, the peroxy acid is extracted. This constitutes a very delicate test for chromate or for hydrogen peroxide. The exact composition of the acid is not known as it is too unstable to isolate, but salts of the acid $HCrO_5$ may be obtained with organic bases such as pyridine; and the ammonium compounds, $(NH_4)_2CrO_5 \cdot H_2O_2$ [or $(NH_4)_2H_2CrO_7$], $(NH_4)_3CrO_8$, and $CrO_4 \cdot 3NH_3$ have been prepared.

Compounds of Molybdenum

17. Valence States.—Molybdenum forms compounds with the positive valence numbers 2, 3, 4, 5, and 6; however, the + 2 and + 4 compounds exist in water solutions only in the form of a few relatively unstable complex ions. Approximate values of the oxidation-reduction potentials for the other valences in acid solution are given below. The value for the oxidation of the metal is based upon the heat of formation of MoO_3 as 167,000 cal.

	Volts
$Mo + 3H_2O = MoO_3 + 6H^+ + 6E^-$	− 0.25
$MoO^{+++} + 2H_2O = MoO_3 + 4H^+ + E^-$	− 0.5
$Mo + H_2O = MoO^{+++} + 2H^+ + 5E^-$	− 0.2
$Mo^{+++} + H_2O = MoO^{+++} + 2H^+ + 2E^-$	> + 0.2

18. Divalent Molybdenum.—The **dichloride,** $MoCl_2$, is formed by heating the trichloride: $2MoCl_3 = MoCl_2 + MoCl_4$. The **bromide** may be prepared in a similar manner, and the iodide by heating the pentachloride in hydrogen iodide. These halides are insoluble in water but dissolve in alkalies, and upon acidifying the solution, precipitate the complex bases $(Mo_3X_4)(OH)_2$. The halides appear to be derivative of the same complex having the formula Mo_3X_6, or $[Mo_3X_4]X_2$.

19. Trivalent Molybdenum.—Solutions of trivalent molybdenum are prepared by the reduction of molybdic acid by powerful reducing agents. The color of the solutions is generally yellow orange. The **hydroxide,** $Mo(OH)_3$, is black, and insoluble in water or excess hydroxide. Upon ignition, it gives the **oxide,** Mo_2O_3. Ammonium sulfide precipitates the **sulfide,** Mo_2S_3, soluble in excess of the reagent. The **phosphate** is also but slightly soluble. Complex ions are formed with halides, and with thiocyanate, e.g. K_3MoCl_6 and $K_3Mo(CNS)_6$; and the colors of these solutions vary from red to violet.

20. Tetravalent Molybdenum.—The **sulfide,** MoS_2, is the principal ore of the element. The **oxide,** MoO_2, forms when the sesquioxide is heated in air, or the trioxide is reduced with hydrogen (500°) or carbon (700°). The chloride, bromide, and iodide may be prepared mixed with the dihalide, by heating the trivalent compound. These compounds are not soluble in water, and the tetravalent ion is not stable, probably being oxidized and reduced to MoO^{+++} and Mo^{+++}. However, a number of water soluble complex cyanide and halide compounds have been prepared, e.g. $K_4Mo(CN)_8$, $K_4MoO_2(CN)_4$, and H_nMoI_{4+n}.

21. Pentavalent Molybdenum.—The **penta chloride,** $MoCl_5$, is made by heating the metal or lower chloride in chlorine. It is the only known oxygen free compound of this valence. In water, it hydrolyzes to the molybdenyl compound: $MoCl_5 + H_2O = MoOCl_3 + 2HCl$. Compounds of the common acids, with MoO^{+++} or MO_2^{+}, are prepared by the reduction of molybdate in acid solution with moderately strong reducing agents, e.g. $SnCl_2$. The addition of hydroxide to the solutions precipitates the **hydroxide,** $MoO(OH)_3$, which may be decomposed to the **pentoxide,** Mo_2O_5. A delicate test for pentavalent molybdenum is the formation of a deep red colored solution upon the

addition of thiocyanate, probably $Mo(OH)_2(CNS)_3$. Mild reducing agents act upon an excess of molybdic acid with the production of a deep blue precipitate, **molybdenum blue,** which appears to be a molybdenyl molybdate, $(MoO)_3(MoO_4)_2$, or $(MoO_2)_2MoO_4$.

22. Hexavalent Molybdenum.—The **trioxide,** MoO_3, is a white solid which is soluble, one part in 500 parts of cold water, forming a slightly acid solution. The oxide is formed by roasting the disulfide in air, by the igniting of ammonium molybdate, or by the decomposition of a molybdate with hot nitric acid. In the latter case, if the solution is allowed to crystallize in the cold, yellow **molybdic acid,** $H_2MoO_4 \cdot H_2O$, separates.

The oxide forms normal **molybdates,** e.g. Na_2MoO_4, especially if fused with basic oxides or carbonates; but these normal salts are in general unstable, if soluble in water, and tend to form **polymolybdates,** e.g. $Na_2Mo_{16}O_{31}$, $K_2Mo_4O_{13}$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. The last compound separates when a solution of the trioxide in ammonia is evaporated, and is usually known as **ammonium molybdate.** Lead and the alkaline earth normal molybdates are but slightly soluble, similar to the sulfates and chromates. The slightly soluble molybdenyl molybdate has been mentioned above.

23. A compound of analytical importance is the **ammonium phospho-molybdate,** $(NH_4)_3PO_4 \cdot 12MoO_3$. It forms as a yellow precipitate, when a solution of ammonium molybdate is added to a solution of orthophosphate in dilute nitric acid. It is readily soluble in ammonia or alkalies and in phosphoric acid, and its solubility is increased in the presence of chloride and many organic acids. Its importance in analytical work lies in its use in separating phosphate from iron and other ions which form slightly soluble phosphates. The composition of the precipitate is approximately as written, but may contain slightly less MoO_3, depending on the conditions of precipitation.

24. Rubidium and thallium phosphomolybdates are likewise insoluble in nitric acid, as are also salts of many of the heavy metals, if the solutions are not too acid. A number of other phosphomolybdate complexes also exist: for example the compound, $(NH_4)_6(PO_4)_2 \cdot 5MoO_3 \cdot 7H_2O$, crystallizes from the solution formed by dissolving the ordinary precipitate in excess ammonia.

Molybdic oxide forms with hydrogen peroxide the **peroxy-acid,** $H_2MoO_5 \cdot nH_2O$, and salts of this or other peroxy-acids have been prepared.

25. The trioxide acts toward strong acids as a basic oxide; with hydrochloric acid it forms the somewhat volatile **oxychloride,** $MoO(OH)_2Cl_2$; and with sulfuric acid the **oxysulfate,** MoO_2SO_4. **Oxybrom** compounds also form, but the iodine compounds are not stable. Fluorine alone forms a **hexahalide,** MoF_6, when the metal is heated in the halogen.

26. Hydrogen sulfide gives with an acid solution of molybdates a precipitate of the **sulfide,** MoS_3. This compound is soluble in excess ammonium sulfide with the formation of **thio-molybdate.**

Compounds of Tungsten

27. Valence States.—Compounds are known containing tungsten with the positive valence numbers 2, 3, 4, 5, and 6. The hexavalent ones alone are of importance. In alkaline solution the tungstates (+ 6) are very stable, but tungstic acid in the presence of hydrochloric acid is reduced by stannous chloride to a blue compound, probably $(WO_2)_2(WO_4)$; and stronger reducing agents, e.g. tin, will reduce the solution to WO^{+++} (green), and upon further action to complex ions of W^{+4}, probably $W(OH)Cl_4^-$ (red brown color), and of W^{+3}, probably $W_2Cl_9^{---}$ (reddish blue). The potential for the oxidation of the metal has been estimated from the heat of oxidation to the trioxide, 195,000 cal.

	$Volts_{25°}$
$W + 3H_2O = WO_3 + 6H^+ + 6E^-$	0.0
$W + 8OH^- = WO_4^{--} + 4H_2O + 6E^-$	+ 1.0
$WO^{+++} + 2H_2O = WO_3 + 4H^+ + E^-$	*ca* − 0.3
$W^{+4} + H_2O = WO^{+++} + 2H^+ + E^-$	*ca* − 0.1

28. Divalent Compounds.—The **halides,** WCl_2, WBr_2, WI_2 have been prepared by the action of reducing agents upon higher halides at high temperatures. The chloride is somewhat soluble in water, but the solution hydrolyzes to some complex substance; the compound $HW_3Cl_7 \cdot 4\frac{1}{2}H_2O$ has been obtained from alcoholic solutions.

29. Trivalent Compounds.—Alkali and ammonia salts, of the general formula, $R_3W_2Cl_9$, have been prepared by the reduction of tungstic acid with tin, but no simple compounds of this valence are known.

30. Tetravalent Compounds.—The **dioxide,** WO_2, is formed by heating the trioxide in hydrogen, but if too high a temperature is employed the oxide is reduced to the metal. The oxide is also a product of the hydrolysis of the tetrachloride, or of tetravalent solutions. It is readily oxidized, and with alkali evolves hydrogen and forms tungstate. It is only slightly soluble in acids. Anhydrous **tetrachloride** and **iodide** may be prepared at high temperatures, but they are readily hydrolyzed by water. The **complex cyanide** ion, $W(CN)_8^{----}$, is stable in water solution, and many of its salts have been prepared. The **sulfide,** WS_2, forms when the trisulfide is ignited. The compound is not soluble in water or dilute hydrogen ion.

31. Pentavalent Compounds.—The **chloride,** WCl_5, and **bromide,** WBr_5, are formed by carefully reducing the hexahalides in hydrogen. The compounds are readily soluble in water, forming light green solutions which contain the ions WO^{+++} or WO_2^{+}; with excess halide the solution appears to form **complex halides** such as $WOCl_5^{--}$.

Similar solutions are formed by the cathodic reduction, or reduction by tin of alcoholic solutions of tungstic acid in hydrochloric acid. When oxalic acid is used, **complex oxalates** are formed, e.g. $Na_3WO_2(C_2O_4)_2$.

The addition of ammonia to the pentavalent solutions precipitates the hydroxide $W(OH)_5$. The pentasulfide is not known.

Stannous chloride gives with tungstic acid a blue precipitate, **tungsten blue,** which is probably a pentavalent tungstate, $(WO_2)_2WO_4$.

32. Hexavalent Compounds.—The yellow trioxide, WO_3, occurs as the mineral wolframochre. It is readily prepared by gently igniting the acid, which is obtained from its salts by digestion with hydrochloric acid. In the cold, the hydrated acid, $H_2WO_4 \cdot H_2O$, separates, while in hot solutions, the anhydrous acid precipitates. The former is somewhat soluble in water, but the latter neither dissolves in water nor any acid, except hydrofluoric.

The trioxide also forms many **polytungstates.** Thus, compounds with sodium oxide of the general formula $(Na_2O)_n(WO_3)_m$ are known, in which, when n = 1, m may vary from 1 to 6; and more complicated compounds in which both n and m are large numbers. Except for a few of the alkali compounds, the

tungstates are not soluble in water. Although the normal sodium salt, $Na_2WO_4 \cdot 2H_2O$, is readily prepared, the commercial "tungstate of soda" is the paratungstate, $Na_{10}W_{12}O_{41} \cdot 28H_2O$. This salt is employed as a mordant in dyeing.

Like molybdenum, the trioxide forms a number of **phosphotungstic** acids. The acid, $H_3PO_4 \cdot 12WO_3$, is used as a reagent to precipitate alkaloids and proteins. The oxide also forms **silicotungstic** acids: e.g. by boiling silica with ammonium polytungstate, the compound, $(NH_4)_8SiW_{10}O_{36} \cdot 8H_2O$, is obtained.

33. When a solution of sodium paratungstate is boiled with hydrogen peroxide, the solution is found to contain the **peroxytungstate,** $NaWO_4 \cdot H_2O$, and more complicated compounds are obtained with sodium peroxide.

34. Tungstates are converted by alkali sulfides into **thiotungstates,** e.g. $(NH_4)_2WS_4$; when these solutions are acidified, the **trisulfide,** WS_3, is precipitated.

35. The **hexahalides,** WF_6, WCl_6, and WBr_6 result from the action of the halogens upon the heated metal. The fluoride is also formed by the reaction: $WCl_6 + 6HF = WF_6 + 6HCl$. The **oxyhalides,** WO_2X_2 and WOX_4, may also be prepared. The fluorides, and also the trioxide, are soluble in excess of fluoride to form complex ions, e.g. $WO_2F_4^{--}$.

Uranium Compounds

36. Valence States.—Uranium shows the same numerous valence states as the other members of the group, but only the tetravalent and hexavalent states are stable in aqueous solutions. Thus a trichloride and a pentachloride may be prepared at high temperatures, but the former is oxidized by water with the evolution of hydrogen, and the latter decomposes in water into tetra and hexa-valent compounds. The dioxide is basic and the trioxide amphoteric, forming with alkalies, uranates, and with acids, uranyl compounds, giving the uranyl ion UO_2^{++}. The oxidation-reduction potential of the metal has been estimated from the heat of formation of the dioxide, 256,000 cal. and other thermal data.

	Volts
$U = U^{++++} + 4E^-$	$+ 1.4$
$U^{++++} + 2H_2O = UO_2^{++} + 4H^+ + 2E^-$	$- 0.41$
$U^{+++} = U^{++++} + E^-$	*ca* $+ 0.7$

37. Tetravalent Compounds.—The **hydrated oxide,** $UO_2 \cdot 2H_2O$,

precipitates when an alkali is added to a uranous solution. The anhydrous oxide may be formed by heating the hydrate, or by reduction of the uranous uranic oxide, U_3O_8, with hydrogen. This oxide is soluble in strong acids forming green solutions of uranous ion. The **tetra-fluoride,** UF_4, may be precipitated from uranous solution by fluoride ion. The other tetra-halides are soluble, however, and the anhydrous chloride may be prepared along with some of the **pentachloride** by the action of chlorine upon the metal, or CCl_4 upon U_3O_4. The **sulfide,** US_2, forms when the elements are heated together around 500°.

38. Hexavalent Compounds.—When uranium ores are extracted with a sulfuric nitric acid mixture, the oxide, U_3O_8, is dissolved to form a yellow solution containing **uranyl ion,** UO_2^{++}. The **trioxide,** UO_3, is difficult to prepare from this solution, as alkalies precipitate alkali uranate. It may, however, be prepared by the decomposition of uranyl nitrate. Upon heating, it forms U_3O_8, and possibly at higher temperatures, U_2O_5.

The uranyl ion forms slightly soluble compounds with phosphates, $UO_2HPO_4 \cdot 4H_2O$, $UO_2NH_4PO_3$; arsenates, $(UO_2)_3(AsO_4)_2$; double alkali carbonates, $UO_2K_4(CO_3)_3$; sulfites, $UO_2SO_3 \cdot 4H_2O$; complex alkali fluorides, $K_3UO_2F_5$; and sulfide, UO_2S. The sulfide is soluble in acid and in ammonium carbonate solution. Uranyl halides, acetate, sulfate, and nitrate are soluble.

Uranyl salts show remarkable fluorescence, and are also subject to photochemical reduction by many organic compounds; for example, uranyl sulfate in sulfuric acid solution is reduced by alcohol in the sunlight to uranous sulfate.

The more common uranates are di-uranates, e.g. $K_2U_2O_7$. They are not soluble in water, but dissolve in acids. The sodium salt, known as uranium yellow, is used in the manufacture of fluorescent uranium glass, and also as a porcelain pigment.

Hydrogen peroxide forms, with uranyl nitrate solution, a precipitate of the **peroxide,** $UO_4 \cdot 4H_2O$; and alkali peroxides form peroxy-uranates, e.g. $Na_2UO_5 \cdot 4H_2O$.

39. Analytical.—In the systematic separation of the metallic elements, chromium and uranium are associated with the aluminum group in that they are not precipitated by H_2S in $0.3N$ H^+, but are precipitated by NH_4OH and $(NH_4)_2S$ as $Cr(OH)_3$ and UO_2S, respectively. When these precipitates are dissolved in nitric acid and treated with sodium peroxide, the

elements remain in solution as Na_2CrO_4 and $UO_4 \cdot 2Na_2O_2$. Chromium may be identified by the precipitation of lead chromate from dilute nitric acid solution, and the uranium may be precipitated from a solution of $UO_2(NO_3)_2$ as $NH_4UO_2PO_4$. The ion, UO_2^{++}, also gives a deep red precipitate with ferrocyanide, $K_2UO_2Fe(CN)_6$.

Molybdenum resembles antimony in that it is precipitated by H_2S in $0.3N$ H^+, and the sulfide is soluble in ammonium sulfide to form the thio-salt. The filtrate from the hydrogen sulfide precipitation, however, is colored blue through the reduction of some of the molybdenum.

In the absence of phosphate, the oxides UO_3 and MoO_3 remain as a residue when their compounds are evaporated with the acids, $HNO_3 + HClO_4$, and the product washed with water. These oxides are soluble in hydrogen fluoride, and the hydrated oxide, H_2WO_4, is not soluble in $2N$ HCl while H_2MoO_4 is.

Tungstate gives a precipitate of tungsten blue with stannous chloride in dilute HCl; and molybdate gives a precipitate of molybdenum blue with stannous chloride in $12N$ HCl, and an orange color (Mo^{+5}) in dilute acid. The Mo^{+5} solution forms, with KCNS, a deep red color of $MoO(CNS)_3$.

In **gravimetric analysis,** the following pure compounds may be separated and weighed: Cr_2O_3, $BaCrO_4$, MoO_3, $PbMoO_4$, WO_3, and U_3O_8. The trioxides of molybdenum and tungsten may be separated by precipitating the mercurous salts, which are then ignited to the oxide.

In **volumetric analysis** dichromate may be titrated against ferrous ion, or an excess of iodide may be added to dichromate in acid, and the iodine titrated with thiosulfate.

Molybdates may be reduced to MoO_2^+ with hydrogen iodide, and the iodine determined with thiosulfate, or the molybdate may be reduced to Mo_2O_3 by zinc, and the product titrated with permanganate.

Uranates may also be reduced with zinc and the solution of UO_2^{++} titrated with permanganate.

CHAPTER XVIII

SUBGROUP VII. MANGANESE

1. Although manganese is one of the more abundant elements, the other two members of Subgroup VII, masurium and rhenium, have but recently been discovered, and exist in such small amounts that their chemistry is virtually unknown. Indeed, almost our only knowledge of these elements is the presence of lines in the X-ray spectrum of certain platinum and columbium compounds, whose frequencies correspond to those calculated for elements of atomic numbers 43 and 75.

The discussion of the relation of atomic structure and valence states of the elements of Subgroup VI is also applicable to manganese except, of course, that it possesses one more electron. In the permanganates, it shows certain resemblances to the perhalates, but in the lower valences it is more closely related to the elements of neighboring atomic numbers. These latter relations are further discussed in Chapter **XIX**.

2. Occurrence.—Manganese is ranked 17th among the elements in order of abundance, the estimated percentage of the lithosphere being 0.08. The principal ore is pyrolusite, MnO_2. Other minerals are braunite, Mn_2O_3; manganite, $Mn_2O_3 \cdot H_2O$; hausmannite, Mn_3O_4; rhodochrosite, $MnCO_3$; alabandite, MnS; hauerite, MnS_2. The manganese ores are generally associated with iron.

3. The Metal.—Manganese is difficult to prepare in the pure state by reduction with carbon, as it forms a series of solid solutions with the carbide, Mn_3C. It is generally prepared by the reduction of the oxide by aluminum. However, all of the manganese consumed in the steel industry is utilized in the form of the iron alloys, **spiegel iron** (15–25 per cent Mn) and **ferromanganese** (70–80 per cent Mn), which are prepared by reducing the mixed ores in the blast furnace.

The pure metal is reddish-gray, and relatively soft compared to iron, but if it contains carbon, it is very hard and brittle. The melting point is lower than those of either iron or chromium. The metal tarnishes readily in moist air; especially if it contains

the carbide, Mn_3C, which evolves methane and hydrogen with water.

The introduction of manganese into steel improves the rolling and forging qualities of the steel and contributes toughness and resistance to wear. It is considered to be the best deoxidizing and desulfurizing agent for steel, this property depending, in part, upon the very slight solubility of the manganous oxide and sulfide in molten iron.

TABLE I

Atomic and Physical Properties of Elements of Subgroup VII

	Mn	Ma	Re
Atomic weight	54.93	98–99	187–188
Atomic number	25	43	75
Isotopes	None	—	—
Electrons in various quantum groups, 1st	2	2	2
2d	8	8	8
3d	8 + 5	18	32
4th	2	8 + 5	32
5th	—	2	18
6th	—	—	8 + 5
7th	—	—	2
Density	7.2	*ca.* 11.5	*ca.* 21
Melting point, °C.	1260	*ca.* 2300	*ca.* 3000
Boiling point, °C.	1900	—	—
Electrical resistivity, ohm-cm.	5×10^{-6}	—	—
Ionization potential of gas atom, volts	7.4	—	—

Manganese bronze contains about 30 per cent manganese in copper. The alloy **manganin** (Cu 84, Mn 12, Ni 4) has a very low temperature coefficient of resistance and is used in electrical instruments.

TABLE II

Reactions of Manganese

$3Mn + 2O_2 = Mn_3O_4$	Heated in air
$Mn + 2H^+ = Mn^{++} + H_2$	
$Mn + 2H_2O = Mn(OH)_2 + H_2$	Slowly in cold
$Mn + X_2 = MnX_2$	X = halogen. F_2 also gives MnF_3
$Mn + S = MnS$	Heated together
$3Mn + C = Mn_3C$	High temperature. With Si forms MnSi and Mn_2Si
$10Mn + 3N_2 = 2Mn_5N_3$	Burns in N_2 at 1200. With P forms Mn_5P_2 and MnP
$2Mn + 4KOH + 3O_2 = 2K_2MnO_4 + 2H_2O$	

4. Reactions of the Metal.—The electro-positive nature (Par. 5) of manganese renders it highly reactive toward oxidizing agents. The principal reactions are given in Table II.

Compounds of Manganese

5. Valence States.—Manganese forms compounds having the positive valence numbers 2, 3, 4, 6, and 7. The two lower valences are basic, the + 4 valence amphoteric, and the two higher valences acidic. The oxidation-reduction potentials relating to the various valence states are summarized below:

	Volts
$Mn = Mn^{++} + 2E^-$	+ 1.1
$Mn^{++} + 2H_2O = MnO_2 + 4H^+ + 2E^-$	− 1.33
$Mn^{++} = Mn^{+++} + E^-$	− 1.5
$Mn^{+++} + 2H_2O = MnO_2 + 4H^+ + E^-$	− 1.2
$MnO_2 + 4OH^- = MnO_4^{--} + 2H_2O + 2E^-$	− 0.71
$MnO_2 + 2H_2O = MnO_4^- + 4H^+ + 3E^-$	− 1.63
$MnO_2 + 4OH^- = MnO_4^- + 2H_2O + 3E^-$	− 0.69
$Mn^{++} + 4H_2O = MnO_4^- + 8H^+ + 5E^-$	− 1.52
$MnO_4^{--} = MnO_4^- + E^-$	− 0.66

A number of very important relations in the chemistry of manganese may be correlated with these values:

Manganic ion, Mn^{+++}, is unstable even at very low concentrations in respect to the decomposition: $2Mn^{+++} + 2H_2O = Mn^{++} + MnO_2 + 4H^+$.

Manganate, MnO_4^{--}, when acidified, decomposes to the dioxide and permanganate: $3MnO_4^{--} + 4H^+ = MnO_2 + 2MnO_4^- + 2H_2O$.

Permanganate in acid solution will oxidize manganous ion to the dioxide, and in alkaline solution will oxidize the dioxide to manganate.

Manganese dioxide in concentrated acid, and permanganate in both concentrated acid and alkali, will slowly evolve oxygen from water. (See Oxidation-reduction Potential of Oxygen.)

Oxygen in normal alkali is not capable of oxidizing the dioxide to manganate, but the reaction does occur in fused potassium hydroxide.

Excess of a reducing agent upon permanganate in acid solutions yields manganous ion; but in alkaline or neutral solution the product is the dioxide. Partial reduction of permanganate in alkaline solution gives manganate, but excess of reducing agent gives the dioxide.

6. Divalent Manganese.—Compounds of this valence are known as manganous. They resemble magnesium and ferrous iron in their solubility relations, and are in general characterized by a delicate pink color. The **hydroxide,** $Mn(OH)_2$, forms when alkali or ammonium hydroxides are added to a manganous solution. Like magnesium hydroxide, it is soluble in ammonium salts. In the air, it quickly darkens through the oxidation to manganic hydroxide, $Mn(OH)_3$, or possibly $MnO \cdot MnO_2 \cdot nH_2O$. When heated in the absence of air, the hydroxide forms the **oxide,** MnO; and this, heated in air, is oxidized to Mn_3O_4.

Alkali and ammonium carbonates precipitate the **carbonate,** $MnCO_3$. This, like the hydroxide, is soluble in excess ammonium ion.

The pink **sulfide,** MnS, though precipitated by soluble sulfides, is readily soluble in dilute acids. The moist solid oxidizes, upon standing in the air, to the sulfate.

The **sulfate, nitrate, halides,** and **cyanide** are soluble; and the last forms the complex ions $Mn(CN)_3^-$ and $Mn(CN)_6^{---}$. The sulfate crystallizes in a number of hydrated forms, a transition from the penta-hydrate to the tetra-hydrate occurring at about 26°. It forms double salts, such as $K_2SO_4 \cdot MnSO_4 \cdot 6H_2O$, isomorphous with the corresponding salts of magnesium.

The **ammonium phosphate,** NH_4MnPO_4, **ferrocyanide,** $Mn_2Fe(CN)_6$, and **oxalate,** $MnC_2O_4 \cdot 2H_2O$, are but slightly soluble, and are of importance in analytical work.

7. Trivalent Manganese.—Reference has been made in the preceding paragraph to the formation of the **hydroxide,** $Mn(OH)_3$, by oxidation of manganous hydroxide. Due to the instability of the manganic ion, Mn^{+++} (Par. **5**), the only compounds which can be prepared from water solutions are slightly soluble, or slightly dissociated.

The **trifluoride** may be prepared by the action of fluorine upon the metal, and the **trichloride** by the decomposition of the tetrachloride. In water, they decompose, e.g. $2MnF_3 + 2H_2O = Mn^{++} + 6F^- + MnO_2 + 4H^+$, but a deep red solution containing the complex fluoride, K_2MnF_5, may be prepared by dissolving the dioxide in excess of potassium acid fluoride. There is evidence of the formation of some H_2MnCl_5 when the dioxide is treated with concentrated hydrochloric acid. The hydroxide in sulfuric acid forms an unstable **sulfate,** and **alums**

have been prepared. Powerful oxidizing agents, e.g. $KMnO_4$, convert manganous ion, in excess acetic acid, into manganic acetate.

8. Tetravalent Manganese.—The chemistry of tetravalent manganese deals largely with the **dioxide,** MnO_2. As the mineral, pyrolusite, it is the most important source of the element. In many respects, the dioxide resembles lead dioxide; and like the latter, although essentially amphoteric, it is comparatively inert toward both acids and bases. In cold concentrated hydrochloric, the oxide dissolves slowly to form a green solution of the **tetrachloride,** and the hydrated dioxide may be reprecipitated from this solution; but upon heating, chlorine is evolved and manganous chloride formed. The sulfate may also be obtained in solution, but it is very unstable toward the evolution of oxygen. A **complex fluoride,** K_2MnF_6, however, is more stable.

The oxide does not dissolve readily in alkali, but **manganites** are formed by fusing the oxide with certain basic oxides. Calcium manganite, $CaMn_2O_5$, is prepared by oxidizing manganous oxide with bleaching powder, and potassium manganite, $K_2Mn_5O_{11}$, by passing carbon dioxide into potassium manganate solution. The oxides, Mn_2O_3, and Mn_3O_4, may be considered as manganous manganites; upon heating, the dioxide loses oxygen to form these oxides or possibly solid solutions of the type $(MnO)_n(MnO_2)_m$.

The oxidation reduction potentials of the dioxide have been discussed in Paragraph **5.**

Manganese dioxide is employed in the paint and varnish industry to catalyse the oxidation of oils by oxygen, i.e. the drying process. The glass industry employs the dioxide to neutralize the green color of ferrous silicate impurities. The largest use (30,000 ton in U. S. in 1926) of the dioxide is as the oxidizing constituent of the ordinary dry cell.

9. " Dry Cells."—The dry Leclanché battery, generally called the "dry cell," consists of a zinc anode, a cathode of carbon packed in manganese dioxide, and an electrolyte of ammonium chloride solution, containing a little zinc chloride, which is held in a porous solid (kieselguhr). The anode reaction is $Zn = Zn^{++} + 2E^-$; and the cathode reaction, $MnO_2 + 4NH_4^+ + Zn^{++} + 2E^- = Mn^{++} + 2H_2O + Zn(NH_3)_4^{++}$. Hence for the total cell reaction, we may write: $Zn + MnO_2 + 4NH_4^+ = Mn^{++}$

$+ Zn(NH_3)_4^{++} + 2H_2O$. The voltage is 1.48. Large currents cannot be drawn from the cell, owing to the polarization of the cathode, possibly due to the slow diffusion of the electrolyte.

10. Hexavalent Manganese.—When manganese dioxide is fused with potassium hydroxide, some decomposition occurs: $3MnO_2 + 2KOH = Mn_2O_3 + K_2MnO_4 + H_2O$. In the presence of air or other oxidizing agents, as potassium chlorate, the manganese is all oxidized to manganate: $2MnO_2 + 4KOH + O_2 = 2K_2MnO_4 + 2H_2O$. The potassium compound is soluble in water, giving a green solution, from which the salt may be crystallized. Manganates are somewhat similar in solubility to sulfates. The free acid cannot be prepared because of the decomposition into the dioxide and permanganate: $3MnO_4^{--} + 4H^+ = MnO_2 + 2MnO_4^- + 2H_2O$; but the very unstable trioxide has been prepared by the reaction: $(MnO_3)_2SO_4 + Na_2CO_3 = Na_2SO_4 + 2MnO_3 + CO_2 + \frac{1}{2}O_2$. Reference should be made to Paragraph **5** for the oxidation-reduction relations of manganate.

11. Heptavalent Manganese.—When the concentration of hydroxide in a manganate solution is decreased, the color changes from green to purple with the formation of permanganate and the dioxide: $3MnO_4^{--} + 2H_2O = 2MnO_4^- + MnO_2 + 4OH^-$. The equilibrium constant for the reaction, as written, is $K = 1.6 \times 10^{-4}$.

The conversion of manganate into permanganate may also be carried out by powerful oxidizing agents in alkaline solution: e.g. $2MnO_4^{--} + ClO^- + H_2O = 2MnO_4^- + Cl^- + 2OH^-$.

A solution of **permanganic acid,** $HMnO_4$, may be prepared by the reaction of dilute sulfuric acid and barium permanganate, or by the oxidation of manganous sulfate by lead dioxide: $2MnSO_4 + 5PbO_2 + 3H_2SO_4 = HMnO_4 + 5PbSO_4 + 2H_2O$. The solution decomposes upon boiling, or in the sunlight. When potassium permanganate is treated with cold concentrated sulfuric acid, the solution turns green through the formation of the sulfate, $(MnO_3)_2SO_4$; and upon the careful addition of cold water, the **heptoxide,** Mn_2O_7, separates as a dark brown, highly explosive liquid.

Alkali permanganates are usually prepared commercially by fusing the dioxide with alkali hydroxide in air to form the manganate, followed by oxidation with chlorine in the alkaline

solution. They may also be prepared by the anodic oxidation of manganate.

If a pure permanganate is desired, the potassium salt is generally employed instead of the sodium salt, as the great solubility of the latter renders it difficult to prepare free from impurities. Alkali permanganates are used as disinfectants (Condy's Liquid), as oxidizing agents in industrial processes, and as volumetric reagents (vide infra).

12. Analytical.—Potassium permanganate is the most widely used oxidizing agent in volumetric analysis. Its importance depends upon its ability to oxidize quantitatively a very large number of substances. These include the direct oxidation to a higher valence of ions or compounds of Fe^{++}, Mn^{++}, Cu^{+}, Sn^{++}, As^{+++}, Sb^{+++}, Ti^{+++}, Mo^{+5}, W^{+5}, U^{+4}, and V^{+4}; the oxidation of the inorganic acids HNO_2, H_2SO_3, H_2S, H_2O_2, and HCNS; the oxidation of organic acids or their salts, such as oxalic and formic acids. In addition to these determinations by direct oxidation, many methods of indirect determinations have been worked out, such as the precipitation of Ca, Sr, Ba, Cu, Pb, Zn, Hg (us), Ce, and La as oxalates, and the subsequent oxidation of the oxalic acid; the determination of phosphate by the precipitation of $(NH_3)_3PO_4 \cdot 12MoO_3$, and the subsequent reduction of the MoO_3 to Mo_2O_3, and reoxidation; the determination of potassium by precipitation with cobalt nitrite and the oxidation of the nitrite; and the standardization of $Na_2S_2O_3$ solution by the addition of a known weight of $KMnO_4$ to excess I^-, followed by the titration of the I_2 liberated by the thiosulfate.

In acid solution, permanganate is reduced to manganous ion: $MnO_4^- + 8H^+ + 5E^- = Mn^{++} + 4H_2O$. Since 5 equivalents of electricity are involved, a one normal (one equivalent of oxidizing power) solution of permanganate is defined as 1/5 molal, when it is to be employed in the above reaction. Commercial potassium permanganate is not of sufficient purity to permit standardization by directly weighing out the salt; hence the solution is generally standardized in terms of one of the following primary standards: sodium oxalate, oxalic acid, pure iron, or ferrous ammonium sulfate, $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$.

One of the advantages of permanganate is that the distinct color change of the reaction serves as an endpoint indicator. However, care must be taken in titrating a reducing agent with

permanganate not to approach the endpoint too rapidly, as excess of the reagent may react with manganous ion to form compounds of Mn^{+3} or Mn^{+4}, which might not be completely reduced.

In alkaline or neutral solutions, permanganate is reduced to the dioxide: $MnO_4^- + 2H_2O + 3E^- = MnO_2 + 4OH^-$; hence a normal solution of permanganate for use under these conditions is defined as 1/3 molal. One of the important applications of this reaction is in the titration of manganous salts in neutral solution: $3Mn^{++} + 2MnO_4^- + 2H_2O = 5MnO_2 + 4H^+$.

In the gravimetric determination of manganese, it may be precipitated as the ammonium manganese phosphate, and ignited to the pyrophosphate. Manganous compounds may also be precipitated as the dioxide by strong oxidizing agents, bromine water frequently being employed. Upon ignition, the dioxide yields Mn_3O_4. Gravimetric determination may also be carried out with the manganous carbonate and sulfide.

In the systematic scheme of qualitative analysis, manganese is associated with the group thrown down by ammonium sulfide (Append. VI). A very delicate confirmatory test is the formation of a purple permanganate color when a very small concentration of manganous is boiled with lead dioxide and concentrated nitric acid.

CHAPTER XIX

IRON, COBALT, AND NICKEL

1. The first "transition series," in which the electrons in the third quantum state (Append. XVIII) are being increased from 8 to 18, is complete with copper; and the three preceding elements, iron, cobalt, and nickel, constitute a triad possessing many common properties, as might be expected from the fact that the differences in structure exist in the lower rather than the outer electron shell.

The free elements are metals of similar appearance, melting point, density, and other physical properties. They show marked resemblance to all the members of the transition series, although a gradual change in properties may be noted between titanium and nickel (Table I).

TABLE I

First Transition Series

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Melting point....	1800	1710	1615	1260	1535	1480	1452	1083	419
Density ...	4.5	5.9	7.1	7.2	7.9	8.9	8.9	8.9	7.1
Principal valences.	3,4(2)	3,4,5	2,3,6	2,4,6,7	2,3(6)	2,3	2,4	1,2	2
Oxides.....	—	—	—	—	—	—	Ni_2O?	Cu_2O	—
	TiO	VO	CrO	MnO	FeO	CoO	NiO	CuO	ZnO
	Ti_2O_3	V_2O_3	Cr_2O_3	Mn_2O_3*	Fe_2O_3	Co_2O_3	Ni_2O_3*	Cu_2O_3	—
	—	—	—	Mn_3O_4	Fe_3O_4	Co_3O_4	Ni_3O_4	—	—
	TiO_2	VO_2	CrO_2*	MnO_2	FeO_2†	CoO_2	NiO_2	—	—
	—	V_2O_5	—	—	—	—	—	—	—
	—	—	CrO_3	MnO_3	FeO_3†	—	—	—	—
	—	—	—	Mn_2O_7	—	—	—	—	—

* This oxide may be a mixture of higher and lower valent oxides.
† Oxide known only in compounds.

The three metals are readily oxidized to the divalent state, but the removal of an additional electron to form the trivalent ion becomes increasingly difficult with increasing atomic number: thus, ferric ion is a good oxidizing agent; cobaltic ion a very

powerful oxidizing agent; and nickelic ion is not known. The divalent ions are similar in properties to the corresponding ions of other elements of the series, especially the adjacent elements, as has been pointed out under chromium and manganese.

Powerful oxidizing agents acting in alkaline solution form salts in which the elements are tetravalent, or, in the case of iron, hexavalent. These are the highest valences shown by the triad and in this respect they are intermediate to chromium and manganese, on the one hand, in which all of the "transition" electrons may be removed, e.g. in chromate and permanganate, and to copper and zinc, on the other hand, in which one and none, respectively, of the electrons of the 18 group may be readily removed. These valence relations are further summarized in Table I.

Another important characteristic of iron, cobalt, and nickel is the tendency to form complex ions. This property has been discussed in Chapter **VII** as related to the very high fields of force existing about the "18 electron kernel" type of ion, and since these transition elements are approaching to this structure, it is not surprising that they also possess this property to a high degree.

A number of relations between iron, cobalt, and nickel, and the corresponding members of the second and third transition series, are discussed in connection with these elements, Chapter **XX**, but in general the "horizontal" periodic relations are more marked than the "vertical," e.g. iron resembles cobalt more than it does ruthenium.

IRON

2. Occurrence.—Iron is probably the most abundant of all the elements. Meteoric material is usually over 90 per cent iron, and this, together with the figure for the density of the earth, indicates that our planet is largely iron, or iron and nickel, with a silicate crust. However, among the elements of the earth's crust (outer ten miles) iron ranks only fourth in abundance, the estimated percentage being 5.06.

The free metal is rarely found on the earth's surface, and then the specimen is generally of meteoric origin. Igneous rocks contain ferrous silicates isomorphous with magnesium silicates as [Mg, Fe]SiO_4 (cf. **XIV**—Table VI); ferric alumino-silicates as

orthoclase, K[Al, Fe]Si_3O_8); and numerous sulfides, the more important being pyrrhotite, $FeS(S)_x$, and pyrites, FeS_2.

The weathering of the igneous rocks has resulted in the formation of deposits of oxides and carbonates which are the commercial source of the metal. The principal ores are: hematite, Fe_2O_3; brown ore, $Fe_2O_3nH_2O$, including limonite, $2Fe_2O_3 \cdot 3H_2O$; magnetite, Fe_3O_4; and siderite, spathic iron or "kidney ore," $FeCO_3$.

In addition to the above, hundreds of minerals are known containing iron in combination with practically all of the acid oxides, and with the sulfides and compounds of other positive elements. Iron is also an essential constituent of the haemoglobin of the blood.

3. Pure Iron.—Iron is tetramorphous; the transition temperatures between the forms are given in Table II. **α-iron, called ferrite,** is a soft, tough, grey-white metal. The crystal lattice is the body-centered cubic type; the metal is highly paramagnetic. The transition from α to β iron does not involve a change in the lattice structure, and appears to be largely electronic in nature, as the unusually high magnetic permeability of α-iron disappears in **β-iron.** The total energy absorbed in the transition is small, and the change appears to start many degrees below the recorded transition point.

TABLE II

Atomic and Physical Properties of Iron

Atomic weight	55.8	Density, 20° C.	7.86
Atomic number	26	Electrical resistivity,	
Isotopes	56, 54	ohm-cm.	10.0×10^{-6}
Electrons in various		Size of the Fe^{++} ion,	
quantum levels, 1st	2	cm. $\times 10^8$ (if Cl^-	
2d	8	$= 1.81$)	0.75
3d	8 + 6	Ionization potential of	
4th	2	gas atom, volts	7.4 ?
Boiling point, °C.	3000	Tensile strength in lbs.	
Melting point, °C.	1535	per sq. in.:	
Transition temperatures:		Iron, cast	13000– 33000
α to β	766	Iron, drawn	50000–100000
β to γ	895	Steel	40000–300000
γ to σ	1400		

γ-iron is but slightly magnetic in comparison to the α-form. Its lattice structure is face-centered cubic. γ-iron forms solid

solutions with iron carbide, and these may be obtained at room temperature in a metastable state by rapid quenching. The importance of this fact is discussed under steel. Little is known regarding the properties of **δ-iron.**

Pure iron is of only slight commercial importance. It may be prepared by heating the oxide in a current of hydrogen, and by the electrolysis of ferrous sulfate solution. In both of these preparations, the iron contains absorbed hydrogen which may be removed by heating in a vacuum. The hydrogen appears to dissolve to form a true solution; the same is true of nitrogen and other gases at higher temperatures.

4. Metallurgy of Pig Iron.—The basic principle involved in the smelting of iron is the reduction of the iron oxides by carbon monoxide. At a comparatively low temperature, ferric oxide is converted completely to the magnetic oxide: $3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$. At higher temperatures this oxide is reduced to ferrous oxide, and then to the metal, but these reactions involve measurable equilibria and are reversible, depending upon the relative pressures of carbon monoxide and dioxide.

TABLE III

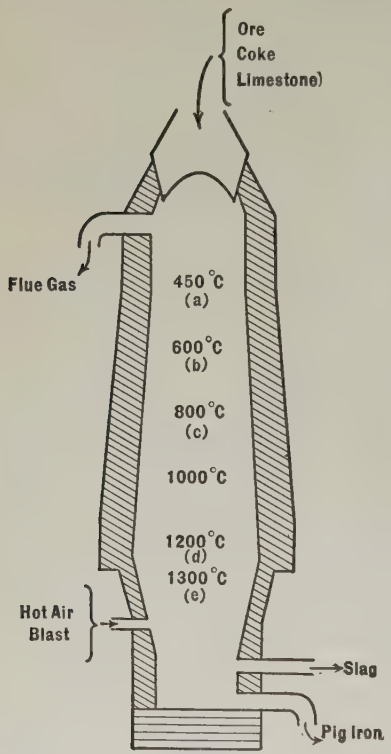
Reactions of Carbon Monoxide and Oxides of Iron

Values for the ratio CO_2/CO at various temperatures

Reaction	Temperature °C.			
	700	800	900	1000
$Fe_3O_4 + CO = 3FeO + CO_2$	0.68	0.55	0.47	0.40
$FeO + CO = Fe + CO_2$	1.68	2.40	3.24	4.17

The modern blast furnace operates so as to carry out these reactions in a continuous manner. The general outline of this furnace is indicated in Figure 1. The dimensions are approximately 22 by 90 ft., and the construction is sheet steel lined with difficultly fusible siliceous fire brick. Only ores with low sulfur and phosphorus content are employed and these may be subjected to a preliminary roasting in order to remove as much sulfur as possible. The ore contains siliceous material, and as all the charge is to be drawn from the furnace in the liquid state, sufficient limestone is added to form an easily fusible calcium

slicate slag. Coke is now universally employed as fuel, and is introduced together with the ore and limestone at the top of the furnace.



(a) $3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$

(b) $Fe_3O_4 + CO = 3FeO + CO_2$

(c) $FeO + CO = Fe + CO_2$ and $CaCO_3 = CaO + CO_2$

(d) Iron melts and $CaO + SiO_2 = CaSiO_3$

(e) $2C + O_2 = 2CO$

Fig. 1.—Blast furnace (diagrammatic).

Dry air, preheated to 425 to 650°, is blown in through a number of water jacketed nozzles or tuyeres near the bottom. The air oxidizes the coke in the lower part of the furnace to carbon monoxide (cf. **XIII—6**). The intense heat of this reaction liquefies the iron which has been reduced in the central part of the furnace by the hot carbon monoxide.

From time to time, the molten metal is drawn off, and either run into molds, or else conveyed directly to Bessemer converters, or open hearth furnaces, and made into steel. The crude iron is called cast iron, or "pig iron," from the shape of the casts made in the old-fashioned furnaces. The impurities present depend

considerably upon the composition of the ore, the nature of the slag, and the temperature at which the furnace has been maintained. The following percentages are representative: C, 2–4.5; Si, 0.7–3; S, 0.1–0.3; P, 0.–3.0; Mn, 0.2–1. In general, a high temperature of reduction increases the percentage of carbon and silicon, but diminishes that of the sulfur through the reaction: $FeS + CaO + CO = Fe + CaS + CO_2$. Practically all of the phosphorus in the charge collects in the iron as Fe_3P.

The melting point of pig iron is about 1150°. The metal is brittle and suitable only for castings not subject to shock. When cooled rapidly, the carbon remains in combination and the product is called **white cast iron;** but when cooled slowly, much of the carbon separates as graphite and the product, known as **grey-cast iron,** is softer and tougher.

Blast furnace slag has the approximate percentage composition: SiO_2, 20–70; CaO and MgO, 25–50; Al_2O_3, 5–20; CaS, 1–4; FeO, 1. In some cases, the composition is such that the slag may be ground and made into cement. Large quantities are also used in paving, in combination with tar.

The **flue gas** contains considerable heat value through its high carbon monoxide content. Part of the gas is burned in the so-called hot-blast stoves, which are used to preheat the air blast, and the rest is employed to develop power about the plant. The gas is generally cleaned from dust before using for power, and the solid obtained contains appreciable quantities of potassium salts, and constitutes a potential source of this alkali.

5. Wrought Iron.—Wrought iron is manufactured from pig iron by oxidizing out the impurities through melting in a reverberatory furnace with iron oxide and a basic flux. As the iron becomes pure, its melting point rises, and the metal collects in lumps which are removed from the furnace. Wrought iron is soft and malleable. It possesses a fibrous structure due to the inclusion of slag, since the temperature of the process is not high enough to melt the pure iron and obtain a good separation from the slag. Wrought iron, while formerly of great importance, is now largely replaced by mild steel.

6. Steel.—Iron which contains from 0.5 to 2.0 per cent carbon and which is capable of being hardened when quenched is called steel. The properties of steel are greatly influenced by small amounts of carbon, as may be best explained by reference to the iron-carbon diagram, Figure 2.

If a molten solution of less than 4.2 per cent of carbon in iron is cooled, the solid which first separates is a solid solution of carbon or iron carbide in γ-iron, called **austenite.** (The diagram also shows a solution in δ-iron above 1450° but this is somewhat uncertain.) At higher concentrations of carbon, the solid phase which separates is **cementite,** Fe_3C. This is metastable in respect to the decomposition into carbon and iron, but the reaction is not rapid. The eutectic of the austenite-cementite phases lies at about 1150°.

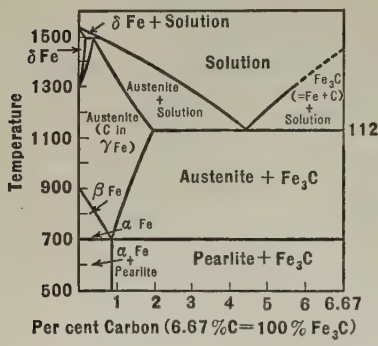


FIG. 2.—The iron-carbon diagram.

Austenite, containing more than 0.9 per cent carbon, upon cooling yields cementite; if it contains less carbon, it yields α or β iron as shown in the diagram. The eutectic temperature is 690°, and the eutectic mixture of α-iron and cementite is known as **pearlite.** However, if austenite is cooled sufficiently rapidly, these transformations do not occur, and the solid solution may thus be obtained at room temperatures as a tough metal of low magnetic susceptibility.

TABLE IV

COMPOSITION AND PHYSICAL PROPERTIES OF SIMPLE CARBON STEELS

Name	Per Cent Carbon	Tensil Strength Lbs. per Sq. In.	Elastic Limit Lbs. per Sq. In.
Very mild	0.05–0.15	45000– 54000	27000–34000
Mild	0.15–0.25	54000– 68000	34000–40000
Low carbon	0.25–0.40	68000– 78000	40000–45000
Medium carbon	0.40–0.60	78000– 90000	45000–55000
Higher carbon	0.60–0.70	90000–100000	54000–64000
Spring	0.70–0.80	100000–105000	64000–72000
Pearlitic	0.85	110000	78000
Hypereutectoid	0.85–1.5	110000– 80000	

The tempering of steel consists in heating a quenched steel, which is largely austenite, or if high in carbon, austenite and

cementite, thus allowing some or all of the austenite to change to α-iron and cementite. The properties of the tempered steel are greatly affected by the temperature of tempering which determines the size of the interlacing crystals. The terms **martensite** and **sorbite** are applied to intermediate stages of the transformation of austenite into pearlite.

7. Many important special steels are made by the addition of elements other than carbon. The presence of other elements greatly modifies the temperature of the iron-carbon phase diagram. Silicon is not only highly soluble in γ-iron, but also catalyses the decomposition of cementite to carbon, thus rendering the steel soft. Nickel forms a complete series of solid solutions with γ-iron, and since the stable form of nickel is the face-centered cubic-lattice like γ-iron, its presence tends to prevent the transformation of the latter into α-iron. The special high speed tool-steels (Par. **19**) which retain their temper at high temperatures also owe their properties, at least in part, to interference with the change of γ into α-iron. Reference should also be made to the metals Mn, Cr, Ni, W, V, and Mo for other special steels.

8. Manufacture of Steel.—The world's production of steel is about 75 million tons, of which almost 50 per cent is produced in the United States. Various manufacturing processes are employed, depending upon the impurities present and the type of steel desired.

(a) *Open-hearth Steel.* The tremendous expansion of the steel industry in the past 50 years was rendered possible through the development of the basic open-hearth process, whereby high-grade steel may be made from pig-iron relatively high in phosphorus and sulfur.

The process consists of heating a charge of pig iron and scrap steel with sufficient iron oxide to oxidize the sulfur, phosphorus, and most of the carbon, in a furnace lined with calcined magnesite or dolomite. The carbon monoxide formed escapes as a gas, while the oxides of sulfur and phosphorus combine with the basic oxides to form a slag. The metal is contained in a shallow hearth (about 40 by 12 feet and 2 feet deep), and the heat is supplied by a gas flame directly over the surface. As mentioned above, the basic oxides also serve as a lining for the hearth. When the desired carbon content is reached, generally after

about 8 hours, the heating is stopped and the melted steel is run into large ladles. Some iron low in sulfur and phosphorus is made into steel by the acid open-hearth process, which is essentially the same as the above, except that the hearth lining is silica.

(b) *Bessemer Steel.* In the Bessemer process, a blast of air is blown through molten pig iron until the impurities are oxidized. The acid process, in which the furnace is lined with silica, is applicable only to iron low in sulfur and phosphorus as these elements are not readily oxidized under these conditions. A basic lining is employed in certain European districts, which permits the removal of the phosphorus in the basic slag; however, the iron must be low in sulfur.

The Bessemer converter is a large egg-shaped vessel mounted on trunnions so as to turn about its shorter axis. The molten metal is poured in through the necklike opening in the top, while the converter is in a horizontal position. The air-blast, which enters through perforations in the bottom, is then turned on, and the converter raised to an upright position. The heats of combustion of the carbon and silicon keep the metal molten in spite of the higher melting point of the pure iron. The "blow" is finished in about ten minutes, and the converter is turned on its side so that a calculated quantity of carbon, manganese, or other metals may be added.

(c) *Crucible and Electrothermal Steel.* The finest grades of tool-steel have long been made by heating wrought iron with pure carbon in small crucibles, and the product is known as crucible steel. Much of the high grade steel is made in small electrically heated furnaces. The method is similar to the open-hearth process, except that the mode of heating permits more careful control.

(d) *Case-hardened Steel.* In the manufacture of armor plate, and many auto and other machine parts, it is often desirable to harden the surface and at the same time keep the toughness of the body of the metal. This is accomplished by heating the article, packed in carbon or in cyanide, until the desired amount of carbon is absorbed into the surface.

9. Reactions of Iron.—Iron is a good reducing agent at ordinary temperature, and a very powerful reducing agent at high temperature, combining readily with all of the negative elements (Table V).

Iron and oxygen do not react in the cold, but when heated they form ferroferric oxide, Fe_3O_4; and at higher temperatures ferric oxide, Fe_2O_3.

The equilibria between iron, iron oxides, and steam are of considerable importance; and the ratios of H_2O/H_2 for the systems, Fe : FeO and FeO : Fe_3O_4, and given in Table V. The solid phases in these systems appear to be solid solutions.

TABLE V

CONSTANTS FOR THE IRON AND STEAM EQUILIBRIA

		700°	800°	900°	1000° C.
$FeO + H_2 = Fe + H_2O$	H_2O/H_2	0.584	0.706	0.822	0.937
$Fe_3O_4 + H_2 = 3FeO + H_2O$	H_2O/H_2	1.45	2.98	5.50	9.12

At lower temperatures the reaction is entirely $3Fe + 4H_2O = Fe_3O_4 + 4H_2$, as ferrous oxide is unstable in respect to iron and Fe_3O_4 below 570°; and at 400°, the ratio H_2O/H_2, in this equilibrium is about 0.2.

The equilibria between iron, iron oxides, and the oxides of carbon have been discussed in connection with the blast furnace, Par. 4.

Iron dissolves in dilute acids with the evolution of hydrogen and the formation of ferrous salts. Strong oxidizing agents yield ferric compounds, but very powerful oxidizing agents, such as concentrated nitric acid or dichromate, render the metal passive; and in this condition it is not dissolved by hydrogen ion nor will it reduce cupric solutions. Passivity is destroyed by scratching the surface, by the action of reducing agents, or by placing the metal in a powerful magnetic field. The phenomenon appears to be due to the formation of a surface film of oxide.

The **rusting** of iron involves two steps: (1) the oxidation to ferrous ion by acid, usually carbonic, i.e. $Fe + 2H_2CO_3 = Fe^{++} + 2HCO_3^- + H_2$ and (2) the formation of ferric oxide (iron rust) by the atmospheric oxygen: $4Fe^{++} + 8HCO_3^- + O_2 + 7H_2O = 2Fe_2O_3 \cdot 3H_2O + 8H_2CO_3$.

The first step does not take place readily with pure iron, due to the over-voltage effect of hydrogen on the metal. Rusting is, therefore, favored by the presence of impurities which present surfaces for the escape of the gas. Pure water is about equal to ferrous ion as an oxidizing agent (Append. II), so there is not much driving power to the solution of the metal in pure water;

the reaction is, of course, favored by increasing the concentration of hydrogen ion.

TABLE VI

REACTIONS OF IRON

$3Fe + 2O_2 = Fe_3O_4$	Readily at 500°, Fe_2O_3 at higher temp.
$Fe + S = FeS$	Heated
$2Fe + 3X_2 = 2FeX_3$	Halogens except I_2 which gives FeI_2
$2Fe + 2H^+ = Fe^{++} + H_2$	Reaction potential + 0.44 volts
$3Fe + C = Fe_3C$	Above 1200°
$Fe + Si = FeSi$	Also Fe_2Si
$3Fe + P = Fe_3P$	
$3Fe + 4H_2O_{(steam)} = Fe_3O_4 + 4H_2$	See Table V
$Fe + 5CO = Fe(CO)_5$	
$Fe + CO_2 = FeO + CO$	See Table III
$4Fe + 2NH_3 = 2Fe_2N + 3H_2$	Fe does not react directly with N_2

COMPOUNDS OF IRON

10. Valence States.—Iron forms two important series of salts: ferrous, with a valence of + 2, and ferric, with a valence of + 3. In addition, salts are known of ferrate ion, FeO_3^{--}, and perferrate ion, FeO_4^{--}, in which iron has, respectively, the valences + 4 and + 6.

Oxidation-reduction potentials relating to the valence states are given below:

	Volts
$Fe = Fe^{++} + 2E^-$	+ 0.44
$Fe + 2OH^- = Fe(OH)_2 + 2E^-$	+ 0.86
$Fe^{++} = Fe^{+++} + E^-$	− 0.74
$Fe(OH)_2 + OH^- = Fe(OH)_3 + E^-$	+ 0.65
$Fe(CN)_6^{----} = Fe(CN)_6^{---} + E^-$	− 0.49
$Fe^{+++} + 4H_2O = FeO_4^{--} + 8H^+ + 3E^-$	*ca.* − 1.7
$Fe(OH)_3 + 5OH^- = FeO_4^{--} + 4H_2O + 3E^-$	*ca.* − 0.9

It follows from these values that the reaction, $Fe + 2Fe^{+++} = 3Fe^{++}$, is practically quantitative. Also ferrous iron is readily oxidized to ferric in alkaline solution, but much less readily in acid; in fact, acid ferrous solutions are oxidized to ferric only very slowly by the air, as the reaction potential is above that of oxygen to hydrogen peroxide (Append. II), which is the first step of the oxygen reaction. The ferrates and perferrates are such powerful oxidizing agents that they are difficult to prepare, and very unstable.

11. Ferrous Compounds.—Ferrous compounds resemble manganous in their solubilities. The **hydroxide,** $Fe(OH)_2$, is precipi-

tated from ferrous solutions by alkalies, but it is only moderately insoluble in water and its solubility is greatly increased in ammonium salts. The pure hydroxide is white, but in the air it quickly turns green, and then reddish-brown through oxidation to ferric hydroxide. The **oxide**, FeO, may be prepared by heating the oxalate, but the product contains some iron and ferric oxide. It burns when heated in air. Ferrous ion has a pale green color.

Ferrous sulfide forms through the direct union of the elements. It precipitates as a black powder when soluble sulfides are added to neutral or basic ferrous solutions, but is readily soluble in acids. The naturally occurring sulfide generally contains an excess of sulfur in solid solution. Ferrous sulfide combines with sulfur to form the **disulfide**, FeS_2, known as **iron pyrites** or "fools' gold." It occurs in nature as brass colored cubic crystals. It is not dissolved by dilute acids, but is slowly decomposed by concentrated hydrochloric acid, $FeS_2 + 2HCl = FeCl_2 + H_2S + S$, and rapidly by nitric acid with the oxidation of the sulfur. An orthorhombic modification called **marcasite** also occurs. Pyrite is an important source of sulfur for the manufacture of sulfuric acid.

Ferrous sulfate, $FeSO_4$, is the most important ferrous salt. It is prepared commercially by the oxidation of moist pyrites: $2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4$. The hydrate, $FeSO_4 \cdot 7H_2O$, which crystallizes upon evaporation of the water solution, is known as green vitriol or copperas. It is used as a disinfectant, in the manufacture of dyes, and in the preparation of ink.

The common black or blue **inks** contain the ferrous salt of gallotannic acid. This is not colored, but upon exposure to the air the black ferric salt is precipitated. A black or blue dye gives the initial color of the ink.

Ferrous ammonium sulfate, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, may be crystallized from equimolar solutions of the two sulfates. This salt is very stable toward oxidation by the air, and is employed as a primary standard in quantitative analysis (cf. **XVIII—12**).

Ferrous carbonate, $FeCO_3$, is readily precipitated from ferrous solutions by soluble carbonates. It occurs in nature as the mineral, siderite.

Ferrous halides are readily soluble in water. They may be prepared by various methods, e.g. by dissolving the metal in the halogen acid, or by the action of the halogen upon excess of the metal.

Ferrous oxalate, FeC_2O_4, forms as a yellow precipitate upon the addition of oxalate to a ferrous solution. With excess reagent, it dissolves with the formation of a yellowish red solution containing the complex ion, $Fe(C_2O_4)_2^{--}$.

Aqueous solutions of ferrous ion absorb nitric oxide with the formation of the **ferronitroso complex ion,** $FeNO^{++}$. This is the basis of the "ring test" for nitrates (cf. **XII—39**).

The complex **ferrous cyanides** are discussed in Paragraph **13**.

12. Ferric Compounds.—Ferric oxide, Fe_2O_3, **hematite,** and its hydrates, $Fe_2O_3 \cdot nH_2O$, "brown ore," are the most important ores of iron. In the various complex minerals containing this oxide, it generally behaves as an acid oxide, its salts being known as **ferrites.** One of the most common of these compounds is **ferrous ferrite** or **magnetite,** Fe_3O_4, i.e. $Fe(FeO_2)_2$. As its common name indicates, it is highly magnetic, and large specimens are known as "lode stones." Ferrites may be prepared by fusing ferric oxide with basic oxides, e.g. $NaFeO_2$, $Ca(FeO_2)_2$, and **ferrous acid,** $HFeO_2$, is obtained by the action of water upon sodium ferrite.

Around 3000° ferric oxide loses oxygen to form magnetite, but at lower temperatures, about 1300°, the reaction is slowly reversed: $4Fe_3O_4 + O_2 = 6Fe_2O_3$.

Finely divided ferric oxide under the names **"rouge"** and **"Venetian red,"** is used as an abrasive and as a pigment.

Ferric hydroxide, $Fe_2O_3 \cdot nH_2O$, usually written $Fe(OH)_3$, is precipitated from ferric solution by alkali and ammonium hydroxides, and carbonates. It is a weak base, and in water solution shows but slightly the acid properties exhibited by the oxide in its mineral compounds, in that it is not soluble in excess of dilute alkali, and only slightly in concentrated alkali. When formed in the cold, the precipitate is often colloidal in nature but is coagulated somewhat by boiling and by the addition of salts, especially those with di- and trivalent anions, since the colloid is positively charged.

Due to the weak basic properties of ferric hydroxide, ferric salts are highly hydrolyzed, and their characteristic yellow brown color in solution appears to be due to the colloidal hydroxide or to basic ions. When this is repressed by acid, the yellow color becomes lighter.

Ferric halides, except the iodide, may be prepared by the action

of the halogen upon the metal, or by dissolving the hydroxide in acid. Iodide ion is oxidized by ferric ion: $2Fe^{+++} + 2I^- = 2Fe^{++} + I_2$. The halides are very soluble, forming many hydrates. With excess of halide ion, they form **complex halides**; and many of the complex salts are known, e.g. Ke_3FeF_6 and $(NH_4)_2FeCl_4$.

Hydrogen sulfide in acid solution reduces ferric salts to ferrous with the precipitation of sulfur, but if ammonium sulfide is used, **ferric sulfide**, Fe_2S_3, is precipitated. The pure compound is unstable, but ferric sulfide complexes with other metallic sulfides occur in nature.

Ferric sulfate, $Fe_2(SO_4)_3$, and **ferric nitrate**, $Fe(NO_3)_3$, are both soluble, but tend to form basic salts by hydrolysis. The former, like most trivalent sulfates, forms **alums**, e.g. $KFe(SO_4)_2 \cdot 12H_2O$.

Ferric phosphate, $FePO_4$, is a common constituent of phosphate rock. It is very slightly soluble, and may be precipitated from an acetic acid solution of ferric ion. It is, however, soluble in strong acids.

Ferric ion, like the ferrous, also forms a **complex oxalate ion**, $Fe(C_2O_4)_3^{---}$, which accounts for the use of oxalic acid in removing ink and iron rust spots from fabrics.

13. Complex Iron Cyanides.—Both ferrous and ferric ion form complex ions with excess cyanide, the former yielding **ferrocyanide**, $Fe(CN)_6^{----}$, and the latter **ferricyanide**, $Fe(CN)_6^{---}$. These complex ions are so stable that their solutions show virtually none of the properties of the iron or cyanide ions.

Sodium and potassium ferrocyanide, $Na_4Fe(CN)_6 \cdot 10H_2O$, and $K_4Fe(CN)_6 \cdot 3H_2O$, are usually prepared as by-products from the distillation of coal. A considerable portion of the nitrogen in coal is liberated as hydrogen cyanide, HCN. This is absorbed in iron oxide purifiers as iron cyanide, which is then treated with lime to form calcium ferrocyanide; this, in turn, is converted into the alkali ferrocyanide. Formerly, the ferrocyanides were prepared by fusing nitrogenous material with potash and iron turnings. The potassium compound is commonly called "**yellow prussiate of potash.**" The hydrates decompose at about 100° yielding colorless powders which ignite when heated in air. With concentrated sulfuric acid the cyanide ion is slowly hydrolysed forming ammonium ion and carbon monoxide: $K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$.

When heated with metallic sodium, the iron is reduced and a mixture of metallic iron and alkali cyanide formed. With hydrochloric acid, the weak **hydroferrocyanic acid,** $H_4Fe(CN)_6$, is formed. This acid may be extracted from concentrated water solution by ether, from which it crystallizes as a colorless compound, stable in dry air, but readily oxidized in moist air.

The ferrocyanide-ferricyanide couple possesses moderately strong oxidizing power (Par. **10**), but ferrocyanides are readily converted into ferricyanides by the action of chlorine in solution. The commercial preparation of **potassium ferricyanide** or **"red prussiate of potash,"** $K_3Fe(CN)_6$, depends upon this oxidation. The ferricyanide ion is not as stable as the ferrous complex, and decomposes slowly in the sunlight.

Alkali ferrocyanides form with ferric ion, first a soluble blue compound, $KFe_2(CN)_6$, and then a very slightly soluble precipitate of **Prussian blue,** $Fe_7C_{18}N_{18}\cdot 10H_2O$, probably $Fe_4[Fe(CN)_6]_3\cdot 10H_2O$ (*vide infra*), which is an important blue pigment. With ferrous ion, potassium ferrocyanide forms a white precipitate of potassium ferrous-ferrocyanide, $K_2Fe[Fe(CN)_6]$. A number of the ferrocyanides are important in analytical chemistry, especially the compounds with zinc and uranium, $Zn_3K_2[Fe(CN)_6]_2$ and $K_2UO_2[Fe(CN)_6]$.

Ferricyanide yields with ferric ion a deep brown solution, probably of undissociated ferric ferricyanide. With ferrous ion a precipitate, Turnbull's blue, is formed. This precipitate is identical in composition to Prussian blue, and is generally considered to be ferric ferrocyanide, although the values for the oxidation reduction potentials predict the formation of ferrous ferricyanide unless the other compound is very much less soluble, as appears to be the case.

Blue print paper is made by treating paper with a solution of ammonium ferricyanide and ferric citrate in the dark. When exposed to light, reduction of the iron by the citrate take place with the formation of Prussian blue. The print is fixed by washing out the unchanged mixture with water.

One of the cyanide groups, in either the ferro- or ferri-cyanide, may be replaced by other groups; e.g. NO, CO, SO_3^{--}, NO_2^-, H_2O, NH_3, AsO_2^-, forming **complex pentacyanides. Sodium ferri-nitrosopentacyanide,** $Na_2FeNO(CN)_5\cdot 2H_2O$, gives an in-

tense blue color with sulfide in alkaline solutions, thus constituting a delicate test for the latter substance.

14. Ferrates and Perferrates.—**Barium** and **strontium ferrate,** $BaFeO_3$, and $SrFeO_3$, have been prepared by heating mixtures of the hydroxide with ferric hydroxide in a current of oxygen. The compounds are decomposed by water, and there is but slight evidence for the formation of the dioxide of iron.

Powerful oxidizing agents in fused alkali or in very concentrated alkaline solution oxidize ferric hydroxide to **perferrate:** e.g. $2Fe(OH)_3 + 10KOH + 3Cl_2 = 2K_2FeO_4 + 8H_2O + 6KCl$. **Barium perferrate,** $BaFeO_4$, analogous to the sulfate, is but slightly soluble and is the most stable of the perferrates. It is not decomposed by water or cold dilute sulfuric acid; but with cold hydrochloric acid, chlorine and oxygen are evolved, though the solution first assumes a red color, probably due to FeO_4^{--}.

15. Iron Carbonyls.—Finely divided iron reacts slowly with carbon monoxide to form the pentacarbonyl, $Fe(CO)_5$, which may be distilled off by heating to 120°. This substance freezes at − 21°, boils at 102°, and decomposes when heated above 200°. In the sunlight it decomposes: $2Fe(CO)_5 = Fe_2(CO)_9 + CO$. The latter carbonyl yields with toluene a green solution containing the **tetracarbonyl,** $Fe(CO)_4$, the analogue of nickel carbonyl.

16. Analytical.—The formation of Prussian blue, through the reaction of ferrocyanide with ferric ion, and ferricyanide with ferrous ion, serve to identify iron in both of the common valence states. Ferric iron may be distinguished also by the deep red color of ferric sulfocyanide, $Fe(CNS)_3$, and a bright red compound with pyrocatechol.

In the scheme for the systematic separation of the elements, iron salts are precipitated by ammonium sulfide and hydroxide as ferrous sulfide. The general method of separation from the other members of this analytical group is indicated in Appendix VI. In case phosphate is present, the analytical procedure requires some modification, because ammonium hydroxide will precipitate ferric phosphate from ferric solutions.

The so-called **basic acetate separation,** which is often used in the iron group, is carried out by the addition of ammonium acetate to a slightly acid solution. Upon heating, hydrolysis occurs; and the precipitate may contain Fe, Ga, Cr, V, W, Al, In, Zr, Ti, as hydroxides, basic acetates, phosphates, or vana-

dates, and the rare earths (if phosphate is present). The method serves to separate these elements from Mn, Zn, Co, Ni, U, alkaline earths, and rare earths (if phosphate is not present), although traces of Zn, Co, Ni, Be, and U may be present in the precipitate.

In gravimetric analysis, iron is usually precipitated as ferric hydroxide by ammonium hydroxide and weighed as ferric oxide. The reagent, **"cupferron,"** $C_6H_5N \cdot NO \cdot ONH_4$, is sometimes used to precipitate iron as the ferric salt. This method has the advantage of precipitating iron (and also Cu, Ti, and Zr) from highly acid solutions, and thus effecting a separation from Al, Cr, Mn, Ni, and Co. When treated with ammonium hydroxide, the precipitate is changed to ferric hydroxide.

Iron is determined in volumetric analysis usually by one of the two reactions: $5Fe^{++} + MnO_4^- + 8H^+ = Mn^{++} + 5Fe^{+++} + 4H_2O$, and $6Fe^{++} + Cr_2O_7^{--} + 14H^+ = 6Fe^{+++} + 2Cr^{+++} + 7H_2O$. In the dichromate method the end-point is determined by removing a drop of the solution and testing with ferricyanide; while in the permanganate method the color of the reagent serves as an end-point indicator. The dichromate method is readily applicable in the presence of chloride, but permanganate tends to evolve chlorine under these conditions, unless an excess of manganous ion is added (cf. **XVIII—12**).

In the preparation of the ferrous solution before titration, ferric iron may be reduced in various ways, but the most generally employed methods are: (1) reduction by passing the solution through a tube containing zinc amalgam (Jones reductor), (2) reduction with stannous chloride followed by removal of excess stannous ion by mercuric chloride.

Ferric salts in solution may also be titrated directly with titanous chloride, using thiocyanate as an indicator: $Fe^{+++} + Ti^{+++} = Fe^{++} + Ti^{++++}$.

COBALT AND NICKEL

17. Occurrence.—Nickel ranks next to iron in abundance in meteoric material, and it seems probable that this order also exists in the interior of the earth. However, on the earth's crust, nickel and also cobalt are classed among the rarer elements.

The commonest cobalt minerals are: smaltite, $CoAs_2$; cobaltite, CoAsS; erythrite, $Co_3(AsO_4) \cdot 8H_2O$; and linnaeite, Co_3S_4.

These ores are generally associated with iron, and often nickel, copper, and silver. The principal source of cobalt is the rich silver-cobalt-nickel veins in Ontario, Canada.

The two most important nickel ores are: pentlandite, $NiS \cdot 2FeS$, and garnierite, $[Ni, Mg]SiO_3 \cdot nH_2O$. Extensive deposits of the former mixed with iron and copper sulfide are found in Ontario, Canada, and of the latter in New Caledonia. Nickel also occurs in other complex sulfides, silicates, arsenides, arsenates, tellurides, oxides, and sulfates. Copper ores usually contain small amounts of nickel, which is removed in the electrolytic refining process.

18. Metallurgy.—The cobalt-silver arsenide ore of Ontario is smelted with a suitable flux in a small blast furnace, yielding crude silver bullion, and a speiss of the arsenides of cobalt, nickel, iron, copper, and some silver. This speiss is subjected to successive roasting processes; with silica to remove iron; with sodium nitrate and carbonate to form sodium arsenate; and with salt to form chlorides of cobalt, nickel, copper, and silver. The soluble chloride is extracted with water; the copper precipitated as the metal by reduction, and the cobalt and nickel precipitated as hydroxides.

The separation of cobalt and nickel is effected by the Mond process (see below), or by the formation of potassium cobaltinitrite (Par. **24**), or chloropentammine cobalti chloride (Par. **24**). The metal is made by reducing the oxide with carbon.

The metallurgy of nickel ores is somewhat similar. The product of the blast furnace smelting is a matte of iron, copper, and nickel sulfides. This matte is freed from much of the iron by oxidizing in a Bessemer converter with a silicate slag.

In the Orford process, the Bessemer matte is fused with carbon and sodium sulfate, which effects a separation of rather pure nickel sulfide in the bottom layer. This sulfide is roasted to the oxide, and reduced by carbon to the metal.

In the Mond process, the matte is roasted to the oxide, reduced to the metal by water gas at 300°, and the nickel removed by volatilization as the carbonyl, $Ni(CO)_4$, in a stream of carbon monoxide at a temperature of 50° to 100°. The carbonyl is then decomposed into the metal and carbon monoxide by heating.

The electrolytic refinement of cobalt and nickel appears to offer advantages in the preparation of pure metals, but the process has not, as yet, received extensive development.

19. The Metals.—The important atomic and physical constants of the metals are given in Table VII. Unlike iron, cobalt and nickel do not have at low temperatures a body centered cubic type of crystal lattice, but are face centered. They do, however, possess magnetic transitions similar to iron; and the non-magnetic forms are isomorphous with the face centered, or γ iron. The metals are silver-grey in color, malleable, and ductile.

TABLE VII

Atomic and Physical Properties of Cobalt and Nickel

	Co	Ni
Atomic weight	58.98	58.69
Atomic number	27	28
Isotopes	None (59)	58, 60
Electrons in various quantum levels, 1st	2	2
2d	8	8
3d	8 + 7	8 + 8
4th	2	2
Density	8.9	8.9
Melting point, °C	1480	1452
Boiling point, °C	2900	2900
Radius of M^{++} in solids, cm. $\times 10^8$ (if Cl = 1.81)	0.72	0.69
Electrical resistivity, ohm-cm	9.7×10^{-6}	6.9×10^{-6}
Tensile strength, lbs. per sq. in	35000 (cast)	150000 (drawn)
Transition temperature, magnetic to non-magnetic form, °C	1150	360

Cobalt does not at present have extensive industrial applications. Its most important use is as a constitutent of the group of alloys known as **stellite,** which contain cobalt and one or more of the metals chromium, tungsten, molybdenum, iron, and nickel. Representative composition of two such alloys are: (1) Co 60, Cr 15, W 20, Mo 5, and (2) Co 30, Fe 52, W 14, Cr 4. These alloys are used as cutting tools in high speed lathes, as they do not lose their edge with heating; and also as surgical instruments, since they may be sterilized in a flame without injury to the edge or polish. Cobalt is also used in making cobalt steel for permanent magnets, the magnetic coercive force being from three to four times that of any other known substance.

The electrolytic nickel plating industry is one of the largest

consumers of nickel. The plated coat is hard, susceptible of high polishing, and is resistant to tarnishing. The electrolyte generally employed is nickel ammonium sulfate.

Finely divided or "active" nickel, prepared by reducing the oxide below 300°, is employed as a catalyst in a number of hydrogenation reactions; the most important commercially being the hardening of fats and oils by their combination with hydrogen, and the conversion of carbon monoxide and steam into carbon dioxide and hydrogen.

Nickel forms an unusually large number of alloys of technical importance (Table VIII), and a large part of the 40 million pounds of the metal consumed yearly in the United States goes into these alloys.

TABLE VIII

NICKEL ALLOYS

Name	Percentage Composition	Properties and Uses
Low nickel steel	Ni 3 to 5, C 0.15, Fe about 96	Armor plate
Invar	Ni 35, Mn 0.5, C 0.5, Fe 64	Low coef. of expansion
Platenite	Ni 46, C 0.15, Fe 54	Glass to metal seals
Monel	Ni 60, Cu 36, Fe 3.5, Al 0.5	Low heat conductivity, casts, non-corroding
Nickel coins	Ni 25, Cu 75	Coins
Constantan	Ni 40, Cu 60	Thermoelements
Manganin	Ni 4, Mn 12, Cu 84	Electrical resistance wire
German silver	Ni 20, Cu 55, Zn 25	Jewelry
Nichrome	Ni 60, Cr 15, Fe 25	Electrical resistance; crucibles
Illium	Ni 62, Cu 7, Cr 22, Mo 8, Fe 1	Acid resisting

20. Reactions of the Metals.—The difficulty of oxidation increases gradually in going from iron to cobalt and nickel (see Par. **21** and Par. **27** for potential values), but in general the reactions of the three metals are similar. Like iron, they are rendered passive by very powerful oxidizing agents. The principal reactions are summarized in Table IX.

TABLE IX

REACTIONS OF COBALT AND NICKEL

$3Co + 2O_2 = Co_3O_4$	
$2Ni + O_2 = 2NiO$	
$M + 2H^+ = M^{++} + H_2$	Slow at 25°. Cf. P. 21 and 27
$M + H_2O = MO + H_2$	Slow at red heat
$3M + 2NO_3^- + 8H^+ = 3M^{++} + 2NO + 4H_2O$	Passive with concentrated acid
$M + X_2 = MX_2$	With halogens. Co also forms CoF_3
$4M + 2NH_3 = M_4N_2 + 3H_2$	400 to 600°
$3M + C = M_3C$	Carbides stable only at temperatures of the molten metals
$M + 4CO = M(CO)_4$	Below 100° but with Co only under pressure
$2M + Si = M_2Si$	Co also forms CoSi, $CoSi_2$, and $CoSi_3$, and Ni forms NiSi and Ni_3Si_2
$M + S = MS$	

COMPOUNDS OF COBALT

21. Valence States.—Cobalt, like iron, forms cobaltous, Co^{++}, and cobaltic, Co^{+++}, ions and compounds, and a few cobaltites, derivatives of the dioxide, CoO_2, which, unlike the corresponding iron oxide, has been prepared. The cobaltic ion is a very powerful oxidizing agent, and for this reason its compounds are not very stable, except those complexes which give a very small concentration of the metal ion. Potential values are summarized below:

	Volts
$Co = Co^{++} + 2E^-$	+ 0.29
$Co^{++} = Co^{+++} + E^-$	− 1.8
$CoO + 2OH^- = CoO_2 + H_2O + E^-$	− 0.9
$Co(CN)_6^{----} = Co(CN)_6^{---} + E^-$	+ 0.3

22. Cobaltous Compounds.—**Cobaltous oxide,** CoO, may be prepared by the reduction of the higher oxides with hydrogen. When heated in air, it forms the cobaltous cobaltic oxide, Co_3O_4. The **hydroxide,** $Co(OH)_2$, is precipitated when alkali hydroxides are added to cobaltous solutions. It is rose-colored, but quickly darkens in the air through oxidation to cobaltic hydroxide.

Cobaltous halides are readily formed by dissolving the hydroxide in the halogen acid. They are soluble and form a number of hydrates. The **chloride** is sometimes used as a "sympathetic ink," by writing with a solution of the pale pink hexahydrate; the characters are invisible but appear upon warming the paper, due to the formation of the blue anhydrous salt. The hexa-

hydrate exists in both red and blue forms. The compound $CoCl_2 3HCl \cdot H_2O$ may be crystallized from a cold solution in hydrochloric acid and alcohol.

The **sulfate** and **nitrate** are soluble and highly hydrated, and the latter readily decomposes to the sesquioxide upon heating.

Cobaltous sulfide is precipitated by sulfide ion in alkaline solution. Like nickel sulfide, it is unusual in that it is not precipitated from acid solutions, but is not soluble, or only very slowly so, in dilute hydrochloric acid.

Sodium bicarbonate precipitates **cobaltous carbonate,** $CoCO_3 \cdot 6H_2O$, at room temperature, and the anhydrous compound at higher temperatures. Basic carbonates are formed by the alkali carbonates.

Cobaltous cyanide, $Co(CN)_2 \cdot 3H_2O$, is but slightly soluble in water, but dissolves in excess of cyanide ion to form a complex **cobaltocyanide** ion, $Co(CN)_6^{----}$ which, however, is readily oxidized to the cobaltic complex.

Cobaltous oxide forms important pigments upon fusion with certain negative oxides. **Smalt,** a deep blue pigment, is really a cobalt glass. **Cobalt blue** is largely cobalt aluminate with more or less zincate. **Cobalt green** is cobalt zincate, and **turquoise green** the same with some chromite.

23. Cobaltic Compounds.—Due to the powerful oxidizing nature of cobaltic ion (Par. **21**), its simple salts are difficult to prepare. The **fluoride,** CoF_3, forms when the metal is heated with fluorine, and the **sulfate,** $Co_2(SO_4)_3 \cdot 18H_2O$, may be prepared by the electrolysis of cobaltous sulfate, followed by fractional crystallization. The sulfate forms **alums.** These, as well as the simple sulfate, are blue in color. Solutions of the fluoride and sulfate readily hydrolyze to the hydroxide, $Co(OH)_3$, which, when ignited in air, forms Co_3O_4.

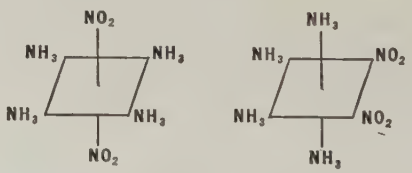
24. Complex Cobaltic Compounds.—The cobaltic ion forms a remarkable number of complex ions in which it possesses a coordination number of six. The formulae of the more important complexes with ammonia, halides, nitrite, and cyanide are given in Table X; and a few of the more familiar compounds are discussed below:

Chloropentamine cobaltichloride, $Co(NH_3)_5ClCl_2$, forms when an ammonical solution of cobaltous chloride is oxidized by air or hydrogen peroxide. As it is but slightly soluble in concen-

trated hydrochloric acid, the dark reddish-violet compound is precipitated from the solution by the addition of this acid. The formation of this compound may be used to separate cobalt from nickel. The great stability of the complex is indicated by the fact that the ammonia is not removed by acid. Only two-thirds of the chloride is precipitated by silver nitrate, but upon standing in contact with silver oxide it is converted into the hydroxide, $[Co(NH_3)_5H_2O](OH)_3$; and when this is dissolved in hydrochloric acid, the **aquapentammine cobaltichloride,** $[Co(NH_3)_5H_2O]Cl_3$, is formed. This compound is not readily soluble in cold water. When the chloropentamine is heated under slight pressure with concentrated ammonia, the **hexammine cobaltichloride,** $[Co(NH_3)_6]Cl_3$, separates as orange colored crystals.

Potassium cobaltinitrite, or potassium hexanitrocobaltate, $K_3Co(NO_2)_6$, is prepared by treating a cobaltous salt with potassium nitrite and acetic acid: $Co^{++} + 3K^+ + 5NO_2^- + 2HNO_2 = K_3Co(NO_2)_6 + NO + H_2O$. The potassium salt is but slightly soluble, and is sometimes employed as a pigment, cobalt yellow. The more soluble sodium salt is employed as a reagent in testing for potassium (cf. **IV—25**). The complex nitrite ion is decomposed by alkalies forming the hydroxides, and by strong acids with the liberation of oxides of nitrogen.

A number of **dinitrotetrammine cobaltic salts** have been prepared. These compounds exhibit isomerism, due to the two possible arrangements of the coordination groups:



Cobaltous ion in the presence of cyanide is readily oxidized, even by hydrogen ion to form the **cobalticyanide,** $Co(CN)_6^{---}$. This ion is very stable, and like the corresponding ferricyanide, forms precipitates with ions of many of the heavier metals.

TABLE X

COBALTIC COORDINATION COMPOUNDS

Cation trivalent
- $[Co(NH_3)_6]X_3$
- $[Co(NH_3)_5H_2O]X_3$
- $[Co(NH_3)_4(H_2O)_2]X_3$

Cation divalent
- $[Co(NH_3)_5Cl]X_2$
- $[Co(NH_3)_5NO_2]X_2$
- $[Co(NH_3)_4H_2O, Cl]X_2$

Cation monovalent
- $[Co(NH_3)_4Cl_2]X$
- $[Co(NH_3)_4Br_2]X$
- $[Co(NH_3)_4(NO_2)_2]X$
- $[Co(NH_3)_4CO_3]X$

Undissociated compounds
- $[Co(NH_3)_3(NO_2)_3]$

Anion monovalent
- $K[Co(NH_3)_2(NO_2)_4]$

Anion divalent
- $K_2[Co(NH_3)(NO_2)_5]$

Anion trivalent
- $K_3[Co(NO_2)_6]$
- $K_3[Co(CN)_6]$

25. Nomenclature of Complex Compounds.—The following system of nomenclature has been proposed by Werner and is in general use:

(*a*) If the complex is a negative ion, the name of the positive ion is first.

(*b*) In giving the structure of the coordination complex, the following order is followed:

(1) Acid radical: Cl^-, chloro; CO_3^{--}, carbonato; CNS^-, thiocyanato; NO_2^-, nitro, etc.

(2) The water or oxygen groups: H_2O, aqua; O^{--}, oxo; O_2^{--}, peroxo; OH^-, hydroxo.

(3) The ammonia groups. Mono, di, tri, etc.—ammine.

(4) Name of positive element. If complex is a positive ion, the following endings are used: univalent, a; divalent, o; trivalent, i; tetravalent, e. If complex is a negative ion, the termination, ate, is added.

(*c*) If the complex is a positive ion, the acid radicals not in the coordination group complete the name. Examples:

$[Co(NH_3)_5Cl]Cl_2$—Chloropentamminecobalti chloride

$K_3[Co(NH_3)_2(NO_2)_4]$—Potassium tetranitrodiammine-cobaltate.

26. Cobalt Dioxide and Cobaltites.—Powerful oxidizing agents in alkaline solution, e.g. hypochlorite and hypoiodite, form the dioxide, CoO_2. The sesquioxide, which is prepared by igniting cobaltous nitrate, is generally considered to be the cobaltous cobaltite, $Co(CoO_3)$, as is also the tricobalt tetroxide, Co_3O_4,

i.e. $2CoO \cdot CoO_2$. Other cobaltites have been prepared by fusing cobaltous oxide with basic oxides in air, e.g. $MgCoO_3$.

Nickel Compounds

27. Valence States.—The principal valence of nickel is + 2. No trivalent salts are known, and the trivalent hydroxide which is frequently mentioned in the literature appears to be the hydrated dioxide. The dioxide is slightly acidic, and a few salts of it have been prepared. There is some evidence for the formation of a monovalent and an octavalent oxide. Potential values are summarized below:

	Volts
$Ni = Ni^{++} + 2E^-$	+ 0.22
$Ni(OH)_2 + 2OH^- = NiO_2 \cdot 2H_2O + 2E^-$	− 0.49
$Ni^{++} + 2H_2O = NiO_2 + 4H^+ + 2E^-$	> − 1.8

28. Nickelous Compounds.—Nickelous compounds are generally green or blue in color, and show many resemblances to cupric compounds. The **hydroxide,** $Ni(OH)_2$, forms as a light green precipitate upon the addition of alkalies to a nickel solution. It is soluble in ammonium hydroxide, due to the formation of the complex nickel ammonia ion which, like the corresponding cupric ion, has a deep blue color. The **oxide,** NiO, results from the direct union of the elements, or from the ignition of the hydroxide or the dioxide. The oxide and hydroxide are readily soluble in acids.

The **halides** are readily soluble, highly hydrated in water, and ammonated in liquid ammonia solutions. The **bromide,** $NiBr_2 \cdot 6NH_3$, is precipitated by the addition of concentrated ammonia to a hot solution of nickel bromide. This property is sometimes utilized in the separation of nickel from cobalt. The **cyanide,** $Ni(CN)_2$, is but slightly soluble in water, but dissolves in excess of cyanide, forming the **complex cyanide ion,** $Ni(CN)_4^{--}$. It differs from the ferrous and cobaltous complex cyanides in that it cannot be oxidized to a nickelic compound.

Below 31°, the **sulfate** crystallyzes as the heptahydrate, $NiSO_4 \cdot 7H_2O$. At higher temperature, two forms of hexahydrated salts are formed, one blue and the other green. **Nickel ammonium sulfate,** $(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$, is used in nickel electroplating. The **nitrate,** $Ni(NO_3)_2 \cdot 6H_2O$, is extremely soluble in water. Alkali carbonates precipitate nickel from solution as

a basic carbonate, but the normal **carbonate,** $NiCO_3 \cdot 6H_2O$, may be precipitated from a solution containing an excess of carbonic acid.

Nickel sulfide, NiS, like cobalt sulfide, is not precipitated from acid solutions by hydrogen sulfide, but is precipitated from ammonia solutions, and the sulfide so formed does not dissolve in dilute hydrochloric acid. The sulfide appears to exist in three modifications. The most soluble modification, which is first formed from alkaline solutions, quickly changes to a form which is less soluble, and also less rapidly soluble, in acid.

29. Nickel Dioxide and Nickelites.—Moderately strong oxidizing agents (Par. **27**) in alkaline solution convert nickelous oxide into the hydrated dioxide. This oxide is an extremely powerful oxidizing agent in acid solution, and readily evolves oxygen under these conditions. **Barium nickelite,** $BaNi_2O_5$, has been prepared by fusing the oxide with barium carbonate. Alkali peroxides form with nickelous salts an oxide of the same general formula as the dioxide, but its reactions indicate that it is the peroxide of divalent nickel.

Hydrated nickel dioxide is the oxidizing constituent of the **Edison storage battery.** The cell reaction upon discharge may be represented by the equation: $Fe + NiO_2 + 2H_2O = Fe(OH)_2 + Ni(OH)_2$. The electrodes are iron and nickel dioxide, and the electrolyte, sodium hydroxide. The potential of the cell is about 1.35 volts at 20°, and depends but slightly upon the concentration of hydroxide, since this substance enters into the cell reaction only so far as it affects the activity of the water.

30. Analytical.—In the systematic scheme for separation of the positive ions (Append. VI), cobalt and nickel are precipitated as sulfides by ammonium sulfide. In the separation from other members of this analytical group, advantage is taken of the slow solubility of the sulfides in cold dilute hydrochloric acid and the non-amphoteric character of the hydroxides. A number of procedures are employed in separating cobalt and nickel; the simplest probably being the precipitation of nickel by dimethylglyoxime, $HON : C(CH_3)C(CH_3) : NOH$, as $Ni(C_4H_7O_2N_2)_2$ from solutions containing acetate and acetic acid. Other methods of separation depend upon the slight solubility of nickel chloride in an ether-hydrogen chloride solution and upon the conversion of cobalt into trivalent compounds, e.g. the precipitation of

cobalt as potassium cobaltinitrite; the precipitation of the sesquioxide, Co_2O_3, by bromine in neutral solution; and the formation of chloropentamminecobalti chloride.

In gravimetric analysis nickel may be weighed as the nickel dimethylglyoxime, after drying at 120°; as the oxide, NiO; or as the metal after electrolytic precipitation. The electrolytic precipitation is made from an ammoniacal solution, and nickel and cobalt are deposited together.

Cobalt is often precipitated as potassium cobaltinitrite, and as the salt of nitroso-beta-naphtol, $Co(C_{10}H_6ONO)_3$. In both procedures, it is weighed as the oxide, Co_3O_4.

CHAPTER XX

PLATINUM AND PALLADIUM METALS

1. The triads: ruthenium, rhodium, palladium; and osmium, iridium, platinum, bear the same relation to the second and third transition series that iron, cobalt, and nickel do to the first (cf. **XIX**).

The six elements of these two series are so similar in properties that the separation of the naturally occurring alloys into the pure metals is not simple, and the commercial term "platinum" generally refers to the whole group.

These elements differ from iron, cobalt, and nickel in their greater nobility, and in their even greater tendencies to form complex ions, or coordination compounds.

Although the similarities in the properties are very pronounced, there are, however, distinct changes in both the horizontal and vertical periodic relations, as is indicated in the following table of valences.

TABLE I

VALENCE RELATIONS

Fe	2, 3, 4, 6	Co	2, 3, 4	Ni	(1), 2, (3), 4
Ru	2, 3, 4, 6, 7, 8	Rh	(2), 3, 4, (6)	Pd	(1), 2, — 4
Os	2, 3, 4, 6, — 8	Ir	(2), 3, 4, 6	Pt	(1), 2, (3), 4, (6)

( ) Very unstable.

Among the more important of these relations which may be pointed out are: the similarity of the hexavalent compounds of iron, ruthenium, and osmium to those of chromium, molybdenum, and tungsten; the similarity of nickel, palladium, and platinum to copper, silver, and gold; the formation of volatile tetroxides by ruthenium and osmium; the remarkable absorption of hydrogen by nickel, palladium, and platinum, and the increasing tendency to form complex ammonia ions shown by the elements on the right.

2. Occurrence.—The important platinum ores are placer deposits in which the metal occurs as small grains or nuggets, the most extensive deposits being those in Russia, Colombia, and Transvaal. The nickel ores of Ontario contain small amounts of platinum as the mineral sperrylite, $PtAs_2$.

Crude native platinum generally contains all of the platinum metals. The following percentage compositions show the usual range: Pt, 60–80; Fe, 5–10; Pd, 1–2; Rh, 0.5–2; Ru, 0.5–2; Os, 1–10; Ir, 1–10. In addition, metal known as osmiridium is found, which contains largely osmium and iridium with small amounts of the other metals.

3. Metallurgy.—Platinum is extracted from sand and gravel by washing and gravity concentration processes similar to those used with gold (cf. **VII**). For the separation of the crude metal into its constituents, it is usually first digested with aqua regia. This dissolves the greater part of the metal, but leaves a residue of any osmiridium, which is fused with zinc in order to render it soluble in acid. The separation of the various metals from the solution then becomes a matter of qualitative analysis (Par. **35**).

4. Properties and Uses of the Metals.—The most important atomic and physical constants are summarized in Table II.

Ruthenium and osmium are grey like iron, while the other metals are more like silver. Osmium has the greatest density of any metal, is brittle, and hard enough to scratch glass. Rhodium and iridium are somewhat softer, and palladium and platinum very malleable. When the metals are formed by the decomposition of their compounds at comparatively low temperatures, they are left in a finely divided or "spongy" condition. Hydrosols, or colloidal solutions, are readily prepared by striking an arc between electrodes of the metals under water.

Spongy palladium and platinum, like nickel, show a remarkable catalytic effect upon many gas reactions. The use of platinum as a catalyst in the manufacture of sulfuric acid, ammonia, and nitric acid, has been mentioned. Platinum causes the instant explosion of a mixture of oxygen and hydrogen, or the ignition of alcohol vapor in air. An electrode coated with finely divided platinum, called platinum black, has a very low overvoltage for hydrogen and other gases, and is often employed in the construction of electrical cells where a reversible gas electrode is desired. The platinum black surface may be prepared by the electrolytic precipitation of the metal from a chloroplatinate solution. Spongy platinum and palladium absorb large volumes of many gases, the absorption of hydrogen by the latter being especially remarkable (Par. **27**).

TABLE II

ATOMIC AND PHYSICAL PROPERTIES

	Ru	Rh	Pd	Os	Ir	Pt
Atomic weight	101.7	102.91	106.7	190.8	193.1	195.23
Atomic number	44	45	46	76	77	78
Electrons in various quantum levels, 1st	2	2	2	2	2	2
2d	8	8	8	8	8	8
3d	18	18	18	18	18	18
4th	8 + 6	8 + 7	8 + 8	32	32	32
5th	2	2	2	8 + 6	8 + 7	8 + 8
6th				2	2	2
Density	12.2	12.5	12.0	22.48	22.4	21.45
Melting point, °C.	2450	1995	1555	2700	2350	1755
Boiling point, °C.	>2700	>2500	2200	>5300	4800	4300
Electrical resistivity, 20° C., ohm-cm. $\times 10^6$	10 ·	5.1	10.8	9	6	10.5

The consumption of the platinum metals in the more important industries is given in Table III. Commercial platinum is usually

TABLE III

CONSUMPTION OF PLATINUM METALS IN U. S.
1925

	Troy Oz.
Jewelry	109000
Dental	24000
Electrical	23000
Chemical	14000

alloyed with the harder metals, especially iridium and rhodium, to make it more durable. Over half of the "platinum metal" employed in the dental industry is palladium. The average price per ounce in 1925 for the pure metals was ruthenium, $85; rhodium, $95; palladium, $78; iridium, $385; and platinum, $118.

5. Platinum, due to its high melting point, incorrodibility, and malleability, is almost indispensable in the manufacture of chemical utensils for high temperature ignitions. Such ware, however, must be handled with some care since it is attacked by a number of reagents, e.g. aqua regia, chlorine solution, ferric chloride, and fused alkalies. It alloys with many metals, especially lead, tin, bismuth, and mercury; and unites with

carbon, phosphorus, sulfur, and silicon, becoming brittle. However, alkali carbonates may be ignited in platinum crucibles without damage. Alloys of palladium and gold, such as "palau", are employed to some extent, as substitutes for platinum in chemical ware.

When pure platinum or platinum iridium alloys are subjected to high temperature for a long period, appreciable loss of weight occurs, doubtless due to the formation of oxide. Platinum rhodium alloys, however, are much less subject to such "volatilization."

6. Reactions of the Metals.—The more important reactions are summarized in Table IV. Reference should be made to the paragraphs dealing with the valence states of each element for approximate potential values. All of the metals exhibit "passivity" with strong oxidizing agents, so that they are not dissolved by as many reagents as the potential values would indicate. (See also Par. 5 for additional reactions of platinum.)

TABLE IV

REACTIONS OF PLATINUM METALS

	Ru	Rh	Pd	Os	Ir	Pt
Spongy metal heated in oxygen	RuO_2 at 700–1200	Rh_2O_3 slowly below 1150°	PdO slowly at 700°	OsO_4 at 200°	IrO_2 slowly at 1050°	PtO slowly at 450°
Spongy metal heated in chlorine	K_2RuCl_5 when KCl is present	$RhCl_3$	$PdCl_2$	$OsCl_4$ at 700°	K_2IrCl_5 when KCl is present	$PtCl_2$ at 360°
Hot HNO_3	Insol.	Insol.	Slowly sol. $Pd(NO_3)_2$	Insol.	Insol.	Insol.
Aqua Regia	H_2RuCl_5	Very slowly soluble H_3RhCl_6	H_2PdCl_4	OsO_4	Very slowly soluble H_2IrCl_6	H_2PtCl_6
Fused with KOH + KNO_3	K_2RuO_4	RhO_2	PdO	K_2OsO_4	Ir_2O_3	$K_2PtO_3 \cdot nH_2O$
Fused with $KHSO_4$	Insol.	$K_2Rh(SO_4)_3$	$PdSO_4$	Insol.	Ir_2O_3	Basic sulfate slowly at 250°

RUTHENIUM COMPOUNDS

7. Valence States.—Ruthenium assumes an unusually large number of different valences, 2, 3, 4, 6, 7, and 8. Compounds of the higher valences in acid solutions are powerful oxidizing

agents, and are reduced to salts of trivalent ruthenium. The reaction, $Ru + 2Ru^{+++} = 3Ru^{++}$, appears to take place as written; but the divalent ion is readily oxidized in air in acid solution. The metal is oxidized in alkaline solution to the hexavalent state (ruthenates), and this is the most stable valence in alkaline solution. No accurate measurements are available regarding the potential values.

	Volts
$Ru = Ru^{++} + 2E^-$	Between 0.0 and − 0.4
$Ru^{++} = Ru^{+++} + E^-$	< − 0.4
$Ru^{+++} + 4H_2O = RuO_4 + 8H^+ + 5E^-$	> − 1.1
$Ru + 8OH^- = RuO_4^{--} + 4H_2O + 6E^-$	< 0.6

8. Divalent Ruthenium.—The fact that the oxide, RuO, does not appear to exist indicates that in alkaline solution this valence is unstable, probably decomposing to give the metal and ruthenate (+ 6).

In acid solution, divalent **halides** may be prepared by the reduction of trivalent compounds by zinc, hydrogen sulfide, or by cathodic reduction. The solution has an azure blue color; solid **cesium ruthenium chloride,** $Cs_3RuCl_5 \cdot 2H_2O$, has been obtained from it, but the salt is rapidly oxidized in air.

Potassium ruthenocyanide, $K_4Ru(CN)_6 \cdot 3H_2O$, is comparatively stable, and forms when ruthenium compounds of higher valence are fused with potassium cyanide. It resembles ferrocyanide in the solubilities of its salts, and is oxidized by chlorine, probably to the trivalent cyanide.

9. Trivalent Ruthenium.—The **chloride,** $RuCl_3$, is formed when the finely divided metal is oxidized by chlorine; the complex chloride, K_2RuCl_5, is readily prepared by the reduction of the tetravalent complex, by alcohol, or other mild reducing agents.

The chloride in solution forms a bright red **ammonia complex,** and with alkalies precipitates the **hydroxide,** $Ru(OH)_3$, which is not soluble in excess of reagent.

The chloride forms a complex with nitric oxide, $RuCl_3NO \cdot H_2O$, and a large number of **alkali complex chlorides** have been prepared, e.g. $K_2RuCl_5H_2O$, $K_2RuNOCl_5$, and also the **nitrite,** $K_2Ru(NO_2)_5$.

The **bromide,** $RuBr_3$, is similar to the chloride in its reactions. The **iodide,** RuI_3, is but slightly soluble, and does not appear to form complex alkali iodides.

10. Tetravalent Ruthenium.—The dioxide, RuO_2, is obtained

by heating the finely divided metal in air. It unites with metal oxides to form **ruthenites,** e.g. $BaRuO_3$. The **sulfate,** $Ru(SO_4)_2$, may be prepared by oxidizing the **sulfide,** RuS_2, with nitric acid or by heating the tetroxide with sulfuric acid. The free tetrachloride has not been prepared; but the potassium ruthenichlorides, K_2RuCl_6 and K_2RuCl_5OH, form when potassium ruthenate is dissolved in cold dilute hydrochloric acid.

11. Hexavalent and Heptavalent Ruthenium.—**Potassium ruthenate,** $K_2RuO_4 \cdot H_2O$, forms when the metal is fused with potassium hydroxide and nitrate. It is soluble in water, forming a deep orange red solution. With cold dilute hydrochloric acid, the complex ruthenichloride is formed, but the **ruthenyl chloride,** RuO_2Cl_2, probably forms as an intermediate step. When acted on by chlorine at 60°, the solution becomes dark green through the formation of perruthenate, RuO_4^-. The alkali salts of the latter have been obtained as black crystals possessing a green metallic luster.

12. Ruthenium Tetroxide.—The tetroxide forms in small quantities by the action of oxygen upon finely divided metal, but is best prepared by the oxidation of an alkaline solution of ruthenate, or by the action of hot nitric acid and perchloric acids on lower valent compounds. The oxide melts at room temperature to an orange liquid, decomposes around 106°, and unlike osmium tetroxide, it is not poisonous. It is somewhat soluble in water, but the oxide seems to possess neither acidic nor basic properties to any marked degree. In acid solution, it is a powerful oxidizing agent.

Osmium Compounds

13. Valence States.—Osmium resembles ruthenium in forming compounds with positive valence numbers, 2, 3, 4, 6, and 8. Oxides and complex ions of the two lower valences are known, but the single ions do not appear to be stable in water solution. The oxidation-reduction potentials are extremely complicated, since almost every negative ion gives a different complex ion with the lower valences. It appears that the tetroxide is reduced directly to the metal by weak reducing agents, e.g. silicon, in the absence of substances which form complex ions with osmium in the lower valence states.

	Volts$_{25°}$
$Os + 4H_2O = OsO_4 + 8H^+ + 8E^-$	-1.3
$OsO_2Cl_4^{--} + 2H_2O = OsO_4 + 4H^+ + 4Cl^- + 2E^-$	-1.0
$OsCl_6^{--} + 2H_2O = OsO_2Cl_4^{--} + 2Cl^- + 4H^+ + 2E^-$	*ca.* -1.2
$OsCl_6^{---} = OsCl_6^{--} + E^-$	-0.5
$Os + 8OH^- = OsO_4^{--} + 4H_2O + 6E^-$	-0.5

14. Divalent Osmium.—The **chloride,** $OsCl_2$, has been prepared by heating the trichloride at 500°, but neither it nor complex chlorides appear to have been prepared in solution. It is claimed that the reduction of the tetroxide with sulfur dioxide yields the **sulfite,** $OsSO_3$; and this, when heated, gives the **oxide,** OsO.

The **complex cyanides,** e.g. $K_4Os(CN)_6$, are probably the most stable compounds of this valence.

15. Trivalent Osmium.—The chloride, $OsCl_3 \cdot 3H_2O$, has been prepared by reducing osmic acid with alcohol in the presence of chloride. When treated with sodium carbonate, the **sesquioxide,** Os_2O_3, is formed.

The following are some of the more important complex salts of this valence: K_3OsCl_6, $K_2OsNOCl_5$, $K_2Os(NO_2)_5$, $KOs(NO)O_2$. The latter compound, called **potassium osmiamate,** is obtained by the action of ammonia on a cold alkaline solution of the tetroxide. It dissolves in hydrochloric acid to form the complex chloride.

16. Tetravalent Osmium.—Chlorine reacts with the metal at about 700° to form the **tetrachloride,** $OsCl_4$. It slowly hydrolyzes in water to the **dioxide,** $OsO_2 \cdot 2H_2O$.

Among the complex salts of this valence are K_2OsCl_6, K_2OsBr_6, K_2OsI_6, and $Na_6OsCl_2(SO_3)_4$.

17. Hexavalent Osmium.—The trioxide is not known, but the metal fused with potassium hydroxide and nitrate gives **potassium osmate,** K_2OsO_4, and this salt is also prepared by reducing an alkaline solution of this tetroxide with alcohol. Barium osmate, $BaOsO_4$, is but slightly soluble. Some hexafluoride forms when fluorine is passed over the metal at 250°. It is decomposed by water.

In acid solution, many complex **osmyl** ions are formed, e.g. $OsO_2Cl_4^{--}$, $OsO_2(C_2O_4)_2^{--}$, $OsO_2(NO_2)_4^{--}$, $OsO_3(NO_2)_2^{--}$, $OsO_3Cl_2^{--}$.

18. Octavalent Osmium.—The volatile **tetroxide,** OsO_4, is formed by direct combustion of the metal in air, or by its oxidation with hot concentrated nitric or sulfuric acids. The vapor has an odor resembling chlorine and is extremely poisonous.

The oxide is soluble in water, but the solution is not acid. Alkalies form weakly bound compounds, e.g. $OsO_4 \cdot 2KOH$, which are readily soluble, and their solution is highly alkaline. As indicated in Par. 13, the oxide is a powerful oxidizing agent.

The **octafluoride,** OsF_8, and probably the **chloride,** $OsCl_8$, form in small amounts when the metal is heated in the halogen. These compounds are highly volatile and hydrolyze to the tetroxide in water.

Rhodium Compounds

19. Valence States.—Rhodium forms compounds with valences of + 3 and + 4, and there is some evidence for the existence of unstable compounds of + 2 and + 6 valences. Rhodic ion, Rh^{+++}, resembles cobaltic ion in the nature of its coordination compounds, and the dioxide is somewhat similar to cobalt dioxide.

	Volts
$Rh = Rh^{+++} + 3E^-$	< -0.4
$Rh(OH)_3 + OH^- = RhO_2 + 2H_2O + E^-$	< -0.8
$Rh^{+++} + H_2O = RhO_2 + 4H^+ + E^-$	> -1.3

20. Trivalent Rhodium.—The **oxide,** Rh_2O_3, results when the metal is heated in air below 1150°. Above that temperature, the oxide decomposes into the metal and oxygen. The hydrated oxide is precipitated from rhodium solutions by alkalies, and is somewhat soluble in excess of concentrated alkali, doubtless with the formation of **rhodites.**

The **trichloride,** $RhCl_3$, may be prepared by heating the metal in chlorine, and the salt so obtained is not soluble in water or acids. However, hydrated chloride formed by dissolving the sesquioxide, in hydrochloric acid, is highly deliquescent. The **bromide,** $RhBr_3$, and **iodide,** RhI_3, have also been prepared. The latter is not readily soluble in hot water. The sulfate, $Rh_2(SO_4)_3$, forms alums. The **sulfide,** Rh_2S_3, is precipitated from acid solutions by hydrogen sulfide; but if excess of hydrogen sulfide is employed, the compound $Rh_2S_3 \cdot 3H_2S$ appears to form, and normal sulfide precipitates but slowly.

The following coordination compounds are analogous to the corresponding cobalt compounds: $K_3[RhCl_6]$, $Na_2[RhCl_5H_2O]$, $[Rh(NH_3)_6]Cl_3$, $[Rh(NH_3)_5Cl]Cl_2$, $K_3[Rh(CN)_6]$, and $K_3[Rh(NO_2)_6]$.

21. Tetravalent Rhodium.—Powerful oxidizing agents in alkaline solution, e.g. ClO^-, convert the sesquioxide into the **dioxide,** RhO_2. The dioxide is not soluble in water or alkalies, but dissolves in hydrochloric acid with the evolution of chlorine. Continued action of sodium hypochlorite on the dioxide gives a blue solution which is thought to contain sodium rhodate, Na_2RhO_4.

Iridium Compounds

22. Valence States.—The important valences of iridium, like those of rhodium, are + 3 and + 4. Powerful oxidizing agents in alkaline solutions form iridates (+ 6), but these are not stable in acid.

	Volts
$Ir = Ir^{+++} + 3E^-$	< -0.4
$Ir^{+++} = Ir^{++++} + E^-$	Between -1.0 and -1.3
$Ir + 8OH^- = IrO_4^{--} + 4H_2O + 6E^-$	< -0.8

23. Trivalent Iridium.—The **trichloride,** $IrCl_3$, forms when the finely divided metal is heated in chlorine. This product is not soluble in water, but the hydrated salt formed by dissolving the sesquioxide in hydrochloric acid is readily soluble. The chloride forms complex salts with the alkali chlorides, e.g. K_3IrCl_6; similar compounds are formed by the **bromide** and **iodide.** These compounds are most readily prepared by reduction of the tetravalent complex salts in acid solution. With alkalies, the **sesquioxide,** Ir_2O_3, is precipitated, and is soluble in excess of the reagent. With hydrogen sulfide in acid solution, the **sulfide,** Ir_2S_3, forms. Iridium **sulfate,** $Ir_2(SO_4)_3$, forms alums. Other important complex salts are the cyanide, e.g. $Na_3Ir(CN)_6$, and **nitrites,** e.g. $K_3Ir(NO_2)_6$.

24. Tetravalent Iridium.—The **dioxide,** IrO_2, is obtained when the finely divided metal is heated to 1100° in air. A hydrated form results from the oxidation of the sesquioxide in air, from the addition of alkalies to the chloroiridates, and upon solution in water of alkali iridates. It is soluble in hydrochloric acid and in sulfuric acid, yielding the **chloride** and **sulfate** in solution. The solid chloride is a dark brown substance very soluble in water and forms stable **complex chlorides,** e.g. K_2IrCl_6. Bromides of this valence are not stable, as bromine is liberated and trivalent iridium is formed.

25. Hexavalent Iridium.—Potassium **iridate,** K_2IrO_3, appears

to be formed when the metal is fused with potassium hydroxide and nitrate, but oxygen is evolved when the salt is dissolved in water and the dioxide precipitated.

Palladium Compounds

26. Valence States.—The principal valences of palladium, like platinum, are + 2 and + 4. A few very unstable compounds of + 3 valence are known, and there is some evidence for the formation of the monovalent chloride upon heating the dichloride, but in general the divalent compounds decompose directly into the metal at high temperatures.

	Volts
$Pd = Pd^{++} + 2E^-$	Between − 0.2 and − 0.5
$PdCl_4^{--} + 2Cl^- = PdCl_6^{--} + 2E^-$	− 1.3

27. Palladium and Hydrogen.—Palladium absorbs hydrogen to a remarkable extent, 600 to 900 times its own volume at 25°, depending somewhat upon the physical condition of the metal. The pressure-concentration curves for the system indicate the formation of a solid solution of the metal and the hydride of empirical formula, Pd_2H; the absorption is accompanied by a considerable increase in the volume of the metal. The gas is almost completely evolved, *in vacuo* at 100°. The hydrogenated metal is a good reducing agent, e.g. reduces mercuric chloride and ferric salts, and also induces the oxidation by oxygen of many carbon compounds, possibly through the formation of hydrogen peroxide: $Pd_4H_2 + O_2 = 4Pd + H_2O_2$; and $H_2O_2 + CO = H_2O + CO_2$.

28. Divalent Palladium.—The **halides** are formed by heating the metal in the halogen. The chloride, $PdCl_2 \cdot 2H_2O$, is soluble in water, and with alkalies gives a precipitate of the oxide, PdO. This is soluble in concentrated ammonia, forming a **complex ammonia** ion, and upon dilution and acidifying slightly with hydrochloric acid, a precipitate of the diammoniate, $PdCl_2 \cdot 2NH_3$, is obtained. The **iodide,** PdI_2, and **cyanide,** $Pd(CN)_2$, are but slightly soluble in water, but dissolve in excess of the precipitating ions. The **sulfide,** PdS, is precipitated from acid solutions by hydrogen sulfide. It is not soluble in ammonium sulfide. The **sulfate** and **nitrate** are readily soluble.

The following types of complex salts have been prepared:

$K_2[PdCl_4]$, $Ag_2[PdCl_2\cdot(OH)_2]$, $K_2[Pd(CN)_4]$, $Na_2[Pd(NO_2)_4]$, $K_2[PdBr_2(NO_2)_2]$, $[PdCl_2\cdot 2CO]$.

29. Tetravalent Palladium.—The dioxide, $PdO_2\cdot nH_2O$ is obtained by anodic oxidation of an acid solution of palladous nitrate. A precipitate of the **sesquioxide,** Pd_2O_3, probably $PdO\cdot PdO_2$, first forms but is decomposed by the acid leaving the dioxide. The dioxide decomposes around 200° to the monoxide.

The tetrachloride and bromide have not been prepared in the pure state, but alkali complexes of the type M_2PdCl_6 are known. The **potassium chloropalladate,** K_2PdCl_6, is prepared by the oxidation of the divalent complex chloride by chlorine, or by dissolving the dioxide in potassium chloride and hydrochloric acid. It is only slightly soluble in cold water and the same is true of the ammonium salt.

Platinum Compounds

30. Valence States.—Platinum forms two important series of compounds of valence + 2 and + 4, and, in addition, a few comparatively unstable compounds of the positive valences 1, 3, and 6. It exhibits strong tendencies to form coordination complexes; and the simple salts are, in general, either insoluble or slightly ionized in solution. For this reason, the oxidation-reduction potentials for the various valence changes depend very much upon the negative ion present.

	Volts$_{25°}$
$Pt + 2H^+ + 4Cl^- = PtCl_4^{--} + 2E^-$	ca − 0.2
$PtCl_4^{--} + 2Cl^- = PtCl_6^{--} + 2E^-$	ca − 0.4

31. Divalent Platinum.—**Platinous chloride,** $PtCl_2$, is generally prepared by heating the tetrachloride or chloroplatinic acid. It also forms when spongy platinum is heated in chlorine at 200°. It is not soluble in water, but dissolves in excess of hydrochloric acid to form a solution of **chloroplatinous acid,** H_2PtCl_4. This acid is most conveniently prepared, however, by the reduction of chloroplatinic acid by sulfur dioxide. The alkali and ammonium salts, e.g. potassium chloroplatinite, K_2PtCl_4, are soluble; but the silver and lead salts are not.

The chloride forms many addition compounds, for example, $PtCl_2CO$ and $PtCl_2\cdot PCl_3$. The **fluoride** is **soluble,** but the

bromide and **iodide** are not. The latter decompose readily: $2PtI_2 = Pt + PtI_4$.

32. Platinous hydroxide, $Pt(OH)_2$, is prepared by boiling chloroplatinites with equivalent quantities of alkali. With excess of alkali, it decomposes, forming the metal and platinates. It is soluble in the halogen acids, but not in oxyacids.

The black **sulfide,** PtS, precipitates when hydrogen sulfide is passed into a solution of chloroplatinite.

The more important coordination compounds of divalent platinum are given below. The **nitroplatinate,** $Pt(NO_2)_4^{--}$, is especially stable, as the platinum is not precipitated by alkalies or hydrogen sulfide, and strong acids form the nitroacid, $H_2Pt(NO_2)_4$.

Platino-Coordination Compounds.

$M_2[PtCl_4]$	$M_2[Pt(CN)_4]$	$[PtCl_2(NH_3)_2]$
$M_2[PtBr_4]$	$M_2[Pt(CNS)_4]$	$[Pt(NH_3)_4]Cl_2$
$M_2[Pt(NO_2)_4]$	$M[PtCl_3 \cdot NH_3]$	$M[Pt(CNS)_3CO]$

33. Tetravalent Platinum.—When platinum is dissolved in aqua regia, **chloroplatinic acid** is formed in solution; and upon removal of nitric acid by excess of hydrochloric acid, the hexahydrate, $H_2PtCl_6 \cdot 6H_2O$, may be obtained by crystallization. The aqua regia solution also contains the **nitrosyl chloroplatinic chloride,** $PtCl_4(NO)_2Cl_2$. By igniting the chloro-acid in an atmosphere of chlorine, the tetrachloride, $PtCl_4$, is obtained. This salt is soluble in water, and when heated to 370° decomposes: $PtCl_4 = PtCl_2 + Cl_2$. The **trichloride** possibly forms as an intermediate step.

The chloroplatinates are the most important compounds of the metal. The silver and cesium salts are very insoluble, and the rubidium, potassium, and ammonium only slightly soluble; hence these compounds are precipitated when the chloro-acid is treated with a solution of the corresponding positive ion.

Platinum tetrabromide and **iodide** are analogous to the chloride.

When the tetrachloride is heated with an excess of sodium hydroxide, **sodium platinate,** $Na_2Pt(OH)_6$, is formed in solution; upon neutralizing this solution with acetic acid the hydrated dioxide, $PtO_2 \cdot 4H_2O$ or $H_2Pt(OH)_6$, is precipitated. The oxide is soluble in the halogen acids, and in sulfuric acid gives a solution of the sulfate, $Pt(SO_4)_2$.

Platinic sulfide, PtS_2, is precipitated from acid solutions of the tetravalent salts by hydrogen sulfide. It is insoluble in nitric acid, but soluble in ammonium polysulfide.

Hundreds of complex **platiniammino-salts** are known in which platinum generally has the coordination number six. Examples of these complex types are: $[Pt(NH_3)_6]X_4$, $[Pt(NH_3)_4X_2]X_2$, and $[Pt(NH_3)X_5]R$.

Nitroplatinites are oxidized by halogens with the formation of **tetranitro dihalidoplatinates,** e.g. $K_2Pt(NO_2)_4Cl_2$. Complex **platinithiocyanides,** e.g. $K_2Pt(CNS)_6$, have been prepared; but the platinocyanides are oxidized to trivalent and not tetravalent complex ions, e.g. $AgPt(CN)_4$.

34. Hexavalent Platinum.—In alkaline solution, the platinates are converted by anodic oxidation into perplatinate, e.g. K_2PtO_4. These compounds are decomposed by sulfuric acid, leaving an insoluble **trioxide,** PtO_3, which readily evolves oxygen upon heating.

35. Analytical.—In the systematic separation of these elements, devised by Noyes and Bray, the platinum metals are separated as follows:

Evaporation with nitric acid removes osmium as volatile tetroxide, and evaporation with mixture of fuming nitric and perchloric acids removes ruthenium as tetroxide. The osmium tetroxide dissolved in sodium hydroxide gives an orange color, $Na_2OsO_5 \cdot H_2O$, and this, with hydrogen sulfide, a black precipitate, Os_2S_3. The ruthenium oxide, dissolved in sodium hydroxide, gives an orange to red solution of $Na_2RuO_5 \cdot H_2O$, which is reduced to the black oxide, Ru_2O_3, by alcohol. In the case of osmium, the alcohol reduction gives an almost colorless solution of Na_2OsO_4.

The addition of 12*N* formic acid to the perchloric acid solution from above precipitates Hg, Au, Pt, Pd, and some Ir and Rh. These metals are dissolved in aqua regia forming $HgCl_2$, $AuCl_4^-$, $PtCl_6^{--}$, $IrCl_6^{--}$, $PdCl_4^{--}$, and $RuCl_6^{---}$, and the gold and mercury extracted by shaking with ethyl acetate. Platinum and iridium are precipitated together as $(NH_4)_2PtCl_6$ and $(NH_4)_2IrCl_6$, and separated by taking advantage of the precipitation of IrO_2, by Br_2 and $NaHCO_3$ from a solution of the chloro-acids. Palladium is precipitated as $(NH_4)_2PdCl_6$ by passing chlorine into the solution of the soluble ammonium chloropalladite, and the

rhodium confirmed by precipitating yellow chloro-pentammino-rhodium chloride $RhCl(NH_3)_5Cl_2$ by heating the solution of $(NH_4)_2RhCl_6$ with 15*N* NH_4OH. This salt is not soluble in 6*N* HCl.

Most of the iridium and rhodium is precipitated with the copper group by hydrogen sulfide in acid solution. This group of sulfides is dissolved in aqua regia; acetic acid and sodium nitrite is added, followed by sodium hydroxide. By this treatment, $Na_3Ir(NO_2)_6$ and $Na_3Rh(NO_2)_6$ remain in solution, while the other elements are precipitated as hydroxides. The complex chlorides are then formed and separated as above.

In quantitative analyses, the elements are generally weighed as metal, though platinum is sometimes weighed as $(NH_4)_2PtCl_6$.

CHAPTER XXI

SCANDIUM, YTTRIUM, AND THE RARE EARTH ELEMENTS

1. Following barium, atomic number 56, there occurs a group of 15 remarkably similar elements known as the Rare Earths, which are trivalent and resemble scandium and yttrium, the two preceeding elements of Main Group III. The existence of this group was long a puzzling problem, as the older forms of the periodic table predicted but one element at this point. The explanation is now given in terms of the electronic structure of the atoms. The distribution of electrons in the various quantum levels in lanthanum, 57, and lutecium, 71, appears to be as follows:

Quantum Level	1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	6_1
Number of Electrons La	2	2	6	2	6	10	2	6	10		2	6	1	2
Number of Electrons Lu	2	2	6	2	6	10	2	6	10	14	2	6	1	2

Up to lanthanum, no electrons have gone into the 4_4 level, as the 5_1, 5_2, and 6_1 quantum levels represent lower energies since, in terms of the Bohr picture, electrons in these highly eliptical orbits are on the average closer to the nucleus. When these levels are occupied, the 4_4 levels then become the next most stable positions, and as 14 electrons are required to fill it, we find this group of 15 elements with the same number of outer or valence electrons, and differing only in the number of electrons in a level comparatively deep within the kernel.

The history of the rare earths dates from the discovery (about 1800) of two earth-like oxides which were given the names yttria and ceria. Further study of these oxides has resulted in the discovery of all the rare earth elements, the final one, illinium, remaining undiscovered until 1926.

Although crude ceria and yttria generally contain at least traces of all the other rare earths, the former consists largely of the oxides of the elements of atomic numbers 57 to 62; and

the latter of oxides of yttrium and the elements 63 to 71; these groups are generally designated as the **Cerium Subgroup** and the **Yttrium Subgroup.**

2. The rare earth elements are so similar that it is extremely difficult, in general, to separate two succeeding elements. There is, however, a gradual change in the properties in going from lanthanum to lutecium; for example, there is a slight decrease in the atomic volume and a corresponding slight decrease in the basic nature of the sesquioxide. Yttrium, being smaller than lanthanum, resembles the heavier members more than it does the lighter ones. Scandium is less basic than yttrium, and resembles aluminum more than the other elements do.

3. Cerium possesses, in addition to the + 3 valence, a well defined + 4 valence; and praseodymium and possibly neodymium form unstable dioxides. Samarium and europium form unstable dichlorides.

4. Compounds of most of the rare earths are highly magnetic (Table I). In completed electron shells, the orientation of the electron orbits appears to be such as to give zero resultant electrical moments, but this is not the case in uncompleted groups. Thus lanthanum ion, La^{+++}, and lutecium ion, Lu^{+++}, are not magnetic; but the transitional elements between are highly so.

TABLE I

PROPERTIES OF SCANDIUM, YTTRIUM, AND THE RARE EARTH ELEMENTS

Atomic Number	Name	Symbol	Atomic Weight	Density	Atomic Volume	Melting Point	Color of Salts	Magnetic Moment (in Weiss units) of M^{+++}
21	Scandium	Sc	45.10	(2.5)	—	1200	Colorless	—
39	Yttrium	Y	89.0	5.57	16.2	1490	"	—
57	Lanthanum	La	138.90	6.16	22.7	826	"	0
58	Cerium	Ce	140.25	6.90	20.3	640	-ic Orange -ous Colorless	11.4
59	Praseodymium	Pr	140.92	6.60	21.3	940	Green	17.8
60	Neodymium	Nd	144.27	6.90	20.9	840	Red	18.0
61	Illinium	Il	—	—	—	—	—	—
62	Samarium	Sa	150.43	7.7	19.5	>1300	Pink	8.0
63	Europium	Eu	152.0?				Rose	17.9
64	Gadolinium	Gd	157.26				Colorless	40.0
65	Terbium	Tb	159.2				"	47.1
66	Dysprosium	Dy	162.52				Yellow	52.2
67	Holmium	Ho	163.5				"	52.0
68	Erbium	Er	167.7				Red	47.0
69	Thulium	Tm	169.4				Green	35.6
70	Ytterbium	Yb	173.6				Colorless	21.9
71	Lutecium	Lu	175.0				"	0

5. Somewhat similar considerations apply to the colors of the rare earth compounds. Ions such as Na^+, Cl^-, La^{+++}, and Lu^{+++}, which contain completed electron groups are colorless; while ions of such as Cr^{+++}, Co^{++}, and most of the rare earths, which belong to transition group, are generally colored. Characteristic absorption lines of the various elements in solutions of their compounds offer an easy method for their detection. The atomic emission spectra are readily excited in the electric arc.

6. Occurrence.—It is estimated that the rare earths constitute only 0.019 per cent of the earth's 10-mile crust. The order of decreasing abundance of the members of the group is given as: Ce, Nd, La, Y, Sa, Gd, Pr, Er, Yb, Lu, Dy, Ho, Tm, Tb, Eu, and Il. It may be observed from this order that the elements of odd atomic numbers are, in general, much less abundant than the even-numbered elements; and that the Yttrium Subgroup is less abundant than the Cerium Subgroup.

The most important source of the Cerium Subgroup is the mineral **monazite,** which is essentially RPO_4 (where R stands for any rare earth element), with generally 4 to 12 per cent of thorium phosphate. Although composed largely of cerium earths, it also contains a few per cent, 1 to 5, of the Yttrium Subgroup. Brazil and Travancore in India are the principal producers of the mineral, which is generally found in alluvial deposits or sands, where it has concentrated due to the high specific gravity of the particles. A phosphate, **xenotime,** which contains largely yttrium earths, also occurs.

Gadolinite is an yttrium silicate of the approximate formula, $Be_2FeY_2Si_2O_{10}$, and cerite is the cerium group silicate, $H_3[Ca, Fe]\text{-}Ce_3Si_3O_{10}$. **Yttrocerite** is a rare earth with calcium fluoride, approximately $RF_2 \cdot CaF_2$, which contains about equal quantities of the two subgroups. Columbates and tantalates, such as **fergusonite,** $(R)_2O_3[Cb, Ta]_2O_5$, are found, often associated with thoria, zirconia, and uranates. Mineral carbonates also occur.

Preparation and Properties of the Metals

7. Due to the highly electropositive nature of the rare earths, the metals are difficult to prepare. The most satisfactory method is the electrolytic reduction of the oxide in the molten fluoride. Reduction with sodium or magnesium generally gives an alloy.

An alloy of the metals of the cerium group is obtained from the rare earth residues of monazite sand, and is called **Misch metal,** or commercially "cerium." It is generally about 70 per cent cerium, and contains some iron. It is highly pyrophoric, i.e. gives sparks if scratched, especially if alloyed with iron, and is used extensively for cigar lighters, gas lighters, etc. During the World War, it was used in tracer bullets and luminescent shells.

The metals of the cerium group, except illinium, have been prepared in fairly pure form; but those of the yttrium group have not, as the higher melting points of these metals and the greater volatility of their chlorides render the electrolytic process difficult of operation.

The melting points and densities are given in Table I. The lower melting metals are about as soft as tin, but the higher melting ones resemble iron. The cerium metals tarnish readily in moist air and ignite when heated. Cerium has a kindling temperature of 165°, neodymium 270°, and lanthanum 445°. The most important reactions are summarized in Table II.

TABLE II

Reactions of Rare Earth Metals

$4M + 3O_2 = 2M_2O_3$	
$2M + 6H_2O = 2M(OH)_3 + 3H_2$	Slow in cold
$2M + 3X_2 = 2MX_3$	X denotes halogen
$2M + N_2 = 2MN$	Forms with oxide when M burns in air
$M + 2C = MC_2$	At high temperature
$2M + 3S = M_2S_3$	
$2M + 3H_2 = 2MH_3$	Reaction at comparatively low temperature
$M = M_{(aq)}^{+++} + 3E^-$	La about + 2.7 volts

Compounds

8. (*a*) **Trivalent.**—Important solubility relations of the cerium and yttrium groups are summarized in Table III. Lanthanum hydroxide is distinctly basic, and the hydroxides of the yttrium group, while less basic, do not dissolve in excess hydroxide. The sulfides, cyanides, simple sulfates, and halides, except fluorides, are all soluble.

Scandium gives a weaker base than any of the yttrium group, but resembles the cerium family in the slight solubility of the

double potassium sulfate. Like aluminum, it forms a complex fluoride ion, ScF_4^-.

TABLE III

Properties of Rare Earth Compounds

	Cerium Group Elements 57 to 62	Yttrium Group Yttrium and Elements 63 to 71
Hydroxides	Somewhat soluble in water	Slightly soluble in water
Carbonates	Not soluble in water nor $(NH_4)_2CO_3$ solution	Not soluble in water; soluble in $(NH_4)_2CO_3$ solution
Oxalates	Not soluble in water nor $(NH_4)_2C_2O_4$ solution	Not soluble in water; soluble in $(NH_4)_2C_2O_4$ solution
Fluorides	Not soluble	Not soluble
Potassium sulfates $K_3R(SO_4)_3$	Not soluble in K_2SO_4 solution	Soluble in K_2SO_4 solution
Nitrates	Soluble in water; less soluble in HNO_3	Soluble in water; less soluble in HNO_3, especially $Gd(NO_3)_3$
Basic nitrates	Somewhat soluble	Slightly soluble
Double nitrates, e.g. $Mg_3R(NO_3)_{12}\cdot 24H_2O$	Easily crystallized	Not readily crystallized
Phosphates RPO_4	Not soluble	Not soluble
Formates	Slightly soluble	Moderately soluble

9. (*b*) **Tetravalent.**—Cerium forms a well defined series of tetravalent compounds, and praseodymium forms a dioxide. Tetravalent cerium is very similar to thorium, and the element is often considered as a member of the fourth periodic group.

Cerium dioxide is formed upon igniting cerous oxide. In acid solution, it is a powerful oxidizing agent:

$$Ce^{+++} + 2H_2O = CeO_2 + 4H^+ + E^-; \text{ About } -1.5 \text{ volts}$$

The hydrated oxide may be formed by the oxidation of cerous hydroxide in alkaline solution, or by the action of alkalies upon ceric salts. It is soluble in nitric, sulfuric, and cold hydrochloric acids, giving the corresponding salts in solution. The chloride solution readily evolves chlorine upon heating. The **fluoride,** $CeF_4\cdot H_2O$, is insoluble in water. It forms complex salts with the alkali fluorides. The **iodate,** $Ce(IO_3)_4$, is slightly soluble, resembling the thorium compound.

TABLE IV

Analysis of Rare Earth Group

(From Noyes and Bray, *Qualitative Analysis for the Rare Elements*).

Precipitate of fluorides of Sc, ‡In, Th, RE. Extract with acid NH_4F.

Solution: NH_4ScF_4. Fume with H_2SO_4

Residue: RE, In, Th as fluorides. Fume with H_2SO_4, add water and NH_4OH, filter out the precipitate, dissolve in $HC_2H_3O_2$, pass in H_2S.

Precipitate, yellow: In_2S_3

Filtrate: RE, Th as acetates. Evaporate, add HNO_3, $KClO_3$ and KIO_3

Precipitate: $Sc_2(SO_4)_3$. Add water and NH_4OH, filter

Precipitate: $Th(IO_3)_4$, $Ce(IO_3)_4$. Add H_2O_2, HNO_3 and KIO_3

Filtrate: other RE. Add NH_4OH, filter, dissolve the precipitate in HCl, add K_2CO_3

Precipitate: $Sc(OH)_3$. Dissolve in HCl, evaporate, add one drop of 27 *N*HF

Residue $Th(IO_3)_4$. Evaporate with HCl, add H_2O_2

Solution $Ce(IO_3)_3$. Add NH_4OH

Precipitate La, Pr, *Nd, *Sm, *Eu and Y subgroup, all as $KRE(CO_3)_2$

Filtrate: Yttrium subgroup: and †Nd, †Sm, †Eu as $KRE(CO_3)_2$. Add HCl, then NH_4OH, filter. Dissolve the precipitate in HCl, evaporate, add $HCHO_2$ and NH_4CHO_2.

Precipitate: $ThO_2 \cdot H_2O_2$

Precipitate, orange: $Ce_2H_2O_2$

Precipitate: Nd, Sm, Eu, ‡Y subgroup

Filtrate: Yttrium subgroup

Precipitate: ScF_3. Add acid NH_4F

Fuse with $NaNO_3$, extract with water, then with $HC_2H_3O_2$ and $NaC_2H_3O_2$.

Solution: NH_4ScF_4

Residue, brown: PrO_2 †La_2O_3 ‡Nd_2O_3

Water extract: *La †Nd †Sm. Add NH_4OH, filter heat precipitate with K_2CO_3

Acetate extract: *Nd *Sm †La ‡Pr Yttrium subgroup

Precipitate: $KLa(CO_3)_2$

Filtrate: Nd, Sm

*A large part, but not all. †A small fraction. ‡All of the element when associated with certain other elements.

Praseodymium dioxide forms when the trivalent nitrate is fused with potassium nitrate at 450°. The oxide is a very powerful oxidizing agent, but is not rapidly decomposed by water. There is some evidence for the existence of neodymium dioxide.

(*c*) **Divalent.**—**Samarium** forms a series of unstable divalent compounds, e.g. $SaCl_2$ and SaI_2, by heating the trivalent halide in hydrogen at 600°. They rapidly evolve hydrogen from water. **Europium** is said to form a divalent chloride which dissolves in water without oxidation.

11. Separation and Analyses.—A fairly satisfactory method of separating scandium, thorium, and most of the members of the cerium subgroup is outlined in Table IV.

The complete separation of the neighboring elements of the yttrium rare earth group can be accomplished only by repeated fractional crystallization or precipitation. Thus, in the original separation of ytterbium and lutecium, 15,000 crystallizations were made.

The yttrium group is commonly divided into three subgroups, and the members of each subgroup are usually separated as indicated below:

Yttrium Group	Terbium Subgroup	Eu, Gd, Tb	Separated by fractional crystallization of double sulfates and ethyl sulfates.
	Erbium Subgroup	Dy, Ho, Er, Tm	Separated by fractional crystallization of ethyl sulfates and bromates.
	Ytterbium Subgroup	Y, Yb, Lu	Separated by fractional crystallization of nitrates in nitric acid, bromates, or double ammonium oxalates.

CHAPTER XXII

THE RADIOACTIVE ELEMENTS

1. The Atomic Nucleus.—The spontaneous disintegration of the heavier elements, that is, their so-called radioactivity, raises many unsolved problems regarding the structure of the atomic nucleus. Little is known of the nature of the force binding the nuclear protons and electrons together. However, the extremely small size of the nucleus suggests a close packing, possibly analogous to the arrangement of atoms in crystals; and the exact determination of atomic masses by Aston and others by the methods of positive ray analysis appears to give a measure of the energy evolved in the formation of the nucleus in terms of the contraction in mass which occurs. Thus, the helium nucleus which presumably contains 4 protons and 2 electrons has not exactly 4 times the mass of 4 protons, but is slightly less, and this difference in the mass is due to the energy lost in its formation (1 gram = 9×10^{20} ergs).

It was early observed that the choice of oxygen = 16, as a basis for atomic weights, gave "whole number" values to the atomic weights of more elements than does the choice of H = 1. This arises through the fact that the mass contraction in the formation of the oxygen nucleus is an excellent mean value for a large number of elements.

The percentage mass contraction (O = 16) for the formation of a number of elements is given in Table I. It will be seen that for the lighter elements the contraction is less than that of oxygen; but the value then becomes greater than oxygen, reaches a maximum in the neighborhood of iron, becoming less than oxygen for the heavy radioactive elements. The maximum contraction at iron is interesting in connection with the great abundance of this element (cf. **XIX—2**).

2. Radioactive "Rays."—Two types of atomic disintegration or radioactive transformations are known: (1) the expulsion of a doubly charged helium atom, called "alpha particle," from the nucleus and (2) the expulsion of one of the nuclear electrons called a "beta particle."

TABLE I

THE PACKING FRACTION IN THE FORMATION OF THE ELEMENTS

From Positive Ray Analysis by Aston

Element	Packing Fraction $\times 10^4$	Mass O = 16	Element	Packing Fraction $\times 10^4$	Mass O = 16
H	(77.8)	1.00778	Cl_{35}	− 4.8	34.983
He	5.4	4.00216	A_{36}	− 6.6	35.976
Li_6	20.0	6.012	Cl_{37}	− 5.0	36.980
Li_7	17.0	7.012	A_{40}	− 7.2	39.971
B_{10}	13.5	10.0135	As	− 8.8	74.934
B_{11}	10.0	11.0110	Br_{79}	− 9.0	78.929
C	3.0	12.0036	Kr_{82}	− 8.8	81.927
N	5.7	14.008	Sn_{120}	− 7.3	119.912
O	0.0	16.0000	I	− 5.3	126.932
F	0.0	19.0000	Xe_{134}	− 5.3	133.929
Ne_{20}	0.2	20.0004	Hg_{200}	+ 0.8	200.016
Ne_{22}	2.2	22.0048	Pb	0.8	206.016
P	− 5.6	30.9825			

The loss of an alpha particle decreases the net nuclear charge, i.e. the atomic number, by two, so that the resulting atom occupies a position in the periodic table two groups lower. On the other hand, the loss of a beta particle increases the atomic number by one, and thus displaces the product to a periodic group one higher than the parent element.

Both of these "rays" are accompanied by enormous energy changes. The alpha particle shot off by Thorium C′ has almost 7 per cent of the velocity of light, and certain beta particles have a velocity of 99 per cent of that of light. The emission of these rays, especially the beta ray, is frequently accompanied by very penetrating light rays called **"gamma rays,"** which have higher frequency than the hardest X-rays. The heavy alpha particles can travel only a few centimeters through air, but in this short distance they produce an extremely large number of ions by impact with the gas molecules. The fastest beta particles can penetrate several millimeters of aluminum. One gram of radium develops 137 cal. of heat per hour, and in its total life is capable of producing heat equivalent to the combustion of half a ton of coal.

Due to their enormous energy, the "radiations" are capable

of bringing about many chemical reactions, such as the decomposition of water. Severe burns are produced by long exposure of living tissue to the rays, but a healing influence is exerted by their action on many diseased tissues; in fact the most important application of the radioactive elements has been in medicine.

3. The Transformation Series.—The radioactive elements, except potassium and rubidium, which possess slight beta activity, are all products of the disintegration of the two parent elements, uranium and thorium. The decomposition of these elements takes place in a series of alpha and beta steps, giving rise to the so-called uranium and thorium transformation series, the final product of each being an isotope of lead. A third series, the actinium series, also exists, which, like the others, ends with lead; but since uranium ores always contain actinium in constant ratio, it is assumed to be a branch of the uranium series, about 3 per cent of the uranium decomposing in this manner.

Beta changes generally take place in pairs, and the second step is usually much more rapid than the first, suggesting that the pairing of electrons occurs in the nucleus. Some of the radioactive elements undergo more than one type of disintegration, thus causing forking in the series. Table II gives a summary of the three series.

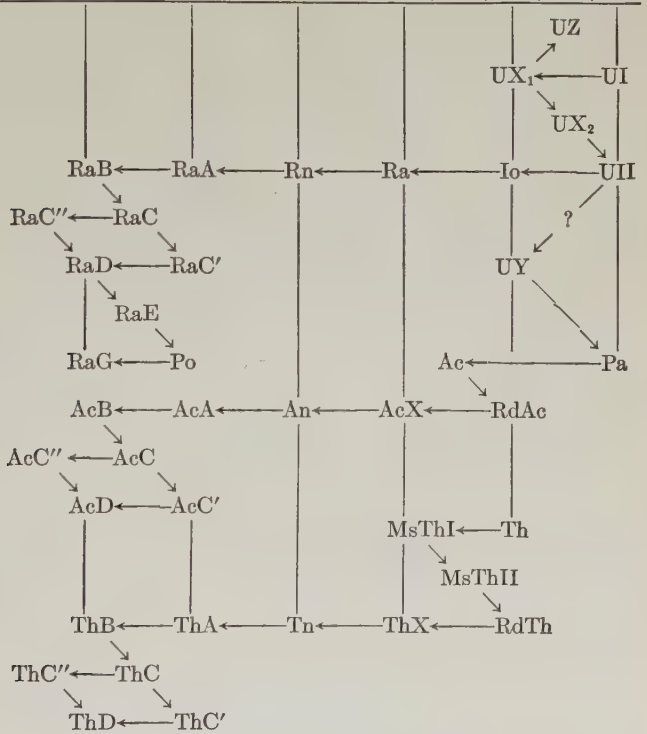
4. Radioactive Constants.—The rate of decomposition is usually expressed by the fraction, λ, of a given quantity, Q, decomposed in a unit time, $\lambda = (1/Q)(dQ/dt)$. The average life, θ, is $1/\lambda$, and the half period, T, i.e. the time required for the transformation of one-half of a given quantity, is 0.69θ. If one element is decomposing to form a second element, which in turn decomposes into a third element, the number of atoms of the first and second elements, N_1 and N_2, when a steady state is reached, is: $N_1\lambda_1 = N_2\lambda_2$. The velocity of the emitted rays is generally expressed relative to that of light, and their penetrating power in cm. of air, aluminum, or lead. An empirical relation of Geiger and Nuttall states that the logarithm of the average life is proportional to the logarithm of the range of the alpha particle in air for a given transformation series.

5. Artificial Disintegration.—Rutherford has found that when high velocity alpha particles are used to bombard some of the lighter elements, nitrogen, for example, a few long range hydrogen

TABLE II

TRANSFORMATION SERIES

Group.....	3′	4′	5′	6′	7′	0	1	2	3	4	5	6
Atomic No..	81	82	83	84	85	86	87	88	89	90	91	92



particles can be detected. The velocity of the hydrogen is so great that it could not have been formed by a collision of an alpha particle with a hydrogen molecule, but appears to have been liberated through the disruption of the nitrogen nucleus.

A number of attempts have been made to convert mercury, atomic number 80, into gold, atomic number 79, by bombarding it with high velocity electrons; but the claims of success which were first made have not been substantiated.

PROPERTIES OF THE RADIOACTIVE ELEMENTS

GROUP VI, ATOMIC NUMBER 92

	Atomic Weight	Half Period	Parent Element	Radiation	Vel. of Particle Rel. to Light	Range, cm., in Air, 0° and 1 Atm.
Uranium I..	238	4.7×10^{9} yrs.		α	0.0456	2.37
Uranium II.	234	2×10^{6} yrs.	UX_2	α	0.0485	2.83

6. The chemistry of uranium has been discussed in Chapter **XVII.** Due to the much longer life period of uranium I, the ordinary preparations of the element consist largely of this isotope, the ratio of the two being 3000 to 1. The atomic weight of ordinary uranium is 238.18, suggesting that possibly an isotope of higher atomic weight also exists.

GROUP V, ATOMIC NUMBER 91

	Atomic Weight	Half Period	Parent Element	Radiation	Vel. of Particle Rel. to Light	Range, cm., in Air, 0° and 1 Atm.
Protoactinium .	230?	6.7 yrs.	UY?	α	0.051	3.314
Uranium X_2...	234	1.65 min.	UX_1	β		
Uranium Z....	234?	6.7 hrs.	UX,	β		

7. Protoactinium is present in all uranium ores, about 7×10^{-8} g. per g. of uranium. As a member of Group V, it resembles its homologue tantalum, atomic number 52, in its chemical properties; in its separation from pitchblende a small amount of tantalum is added to give sufficient quantity of material to work with. So far, it has not been separated from the tantalum mixture. Like tantalum, it is rather electronegative.

The very unstable uranium, X_2, also called brevium, may be separated from its parent element uranium X_1 by taking advantage of the difference in properties of thorium and tantalum. Thus, the mixture treated with hydrogen fluoride forms the slightly soluble UX_1F_4, while the uranium X_2 goes into solution, doubtless as the complex fluoride.

Uranium Z also appears to be a product of uranium X_1, and to give uranium II by a beta decomposition, but these relations have not been definitely established.

GROUP IV, ATOMIC NUMBER 90

	Atomic Weight	Half Period	Parent Element	Radiation	Vel. of Particle Rel. to Light	Range, cm., in Air, 0° and 1 Atm.
Thorium.....	232.12	2.2×10^{10} yrs.		α	0.047	2.58
Ionium.....	230	10^5 yrs.	UII	α	0.048	2.85
Radiothorium	228	1.9 yrs.	MsThII	α	0.053	3.67
Uranium X_1..	234	23.8 days	UI	β		
Radioactinium	226?	18.9 days	Ac	α	0.056	4.36
Uranium Y...	230?	25.5 hrs.	UII?	β		

8. The chemical properties of thorium have been discussed in Chapter **XV**. The isotopes cannot be separated by chemical means, but, for their preparation, advantage may be taken of their different parentage; thus ionium could be prepared free from thorium if a uranium ore free from the latter could be found. So far the purest sample of ionium prepared contains about 70 per cent thorium.

The separation of radiothorium from thorium may be made by frequently adding barium chloride and sulfuric acid to thorium solution over a period of 20 years. In this time, all of the original radiothorium will have disappeared, and the mesothorium I, which would form more radiothorium, is removed as the sulfate.

Uranium Y is the first known member of the actinium series, but its origin from uranium is uncertain.

GROUP III, ATOMIC NUMBER 89

	Atomic Weight	Half Period	Parent Element	Radiation	Vel. of Particle Rel. to Light
Actinium.....	226?	20 yrs.	Pa	β?	
Mesothorium II	221	6.0 hrs.	MsThI	β	0.37–0.7

9. Actinium is separated from uranium ores along with the rare earths, and its isolation from these elements is difficult, especially since the beta radiation, which must be assumed to account for its position in the disintegration series, is too weak to detect; thus, its presence cannot be determined until sufficient time has elapsed to build up its decomposition products. Like the rare earths, the potassium complex sulfate, the fluoride, and oxalate are slightly soluble, though the latter dissolves readily in dilute acids. It is not precipitated by hydrogen peroxide, as is thorium, nor by hydrogen sulfide. The hydroxide is more basic than lanthanum, is only partially precipitated by ammonium hydroxide, and dissolves readily in ammonium salts.

If it becomes possible to separate pure protoactinium, actinium may be readily obtained from this source.

The short life of mesothorium II leads to its presence only in extremely small quantities in thorium.

GROUP II, ATOMIC NUMBER 88

	Atomic Weight	Half Period	Parent Element	Radiation	Vel. of Particle Rel. to Light	Range, cm., in Air, 0° and 1 Atm.
Radium.....	226	1580 yrs.	Io	α	0.05	3.13
Mesothorium I	228	6.7 yrs.	Th	(β)		
Actinium X...	222?	11.2 days	RdAc	α	0.055	4.17
Thorium X...	224	3.6 days	RdTh	α	0.0546	4.08

10. Radium and its isotopes are the heaviest members of the alkaline earth group, and as such, they are very similar in properties to barium. Radium sulfate is less soluble (2.1×10^{-6} g. per 100 g. of water) than barium sulfate, and the hydroxide is more soluble. It is generally separated from barium by the fractional crystallization of the chlorides or bromides, the radium salts being the less soluble.

The commercial sources of radium are unaltered uranium minerals, such as pitchblende, largely U_3O_8, and carnotite, $K_2O(UO_3)_2V_2O_5 \cdot 3H_2O$. The radium content of the unaltered ores is about 3.4×10^{-7} g. per g. of uranium.

The process of extraction depends somewhat upon the type of mineral, but generally involves the precipitation of all the insoluble sulfates and the isolation of the barium and radium

from this precipitate. This may be accomplished by reducing the sulfate to sulfide by carbon, dissolving the product in acid, and precipitating lead and other impurities by hydrogen sulfide. The first extraction of radium was carried out by M. and Mme. Curie. The principal source of radium at present is the rich uranium ores of the Belgian Congo.

Mesothorium I is a constituent of all thorium minerals, but its shorter life renders it less abundant, about 3×10^{-10} g. per g. of thorium. Since the thorium ores contain some uranium, radium is always present in the mesothorium. The commercial extraction from monazite is accomplished in a manner similar to that of radium. Mesothorium I doubtless changes to mesothorium II by a beta change, but the ray is too weak to detect. However, the activity of the mesothorium decomposition products is such that a mesothorium preparation is 240 times more active than the same weight of radium.

Actinium X and thorium X are important only as sources of the very active decomposition products of the two series.

GROUP O, ATOMIC NUMBER 86

	Atomic Weight	Half Period	Parent Element	Radiation	Vel. of Particles Rel. to Light	Range, cm., in Air, 0° and 1 Atm.
Radon	222	3.8 days	Ra	α	0.054	3.94
Thoron	220	54.5 sec.	ThX	α	0.0574	4.74
Actinon	218?	3.9 sec.	AcX	α	0.06	5.40

11. Radon, also called nitron, or radium emanation; thoron, called thorium emanation; and actinon, called actinium emanation, are members of the noble gas family. The latter two, however, are too unstable to be of importance in themselves.

Radon melts at $-71°$, and boils at $-62°$. It is somewhat soluble in water, and very soluble in a number of organic liquids. Small quantities frequently occur in mineral waters. The volume of radon in equilibrium with 1 g. of radium is 6.3×10^{-3} cc. (this quantity is called 1 "curie").

12. Polonium, also called radium F, and its very unstable isotopes are members of Subgroup VI, and hence resemble their homologue, tellurium. In acid solution, polonium forms the ion, Po^{++}, which is a rather powerful oxidizing agent:

$$Po = Po^{++} + 2E^{-}; \quad -0.8 \text{ volts}$$

SUBGROUP VI, ATOMIC NUMBER 84

	Atomic Weight	Half Period	Parent Element	Radiation	Vel. of Particle Rel. to Light	Range, cm., in Air, 0° and 1 Atm.
Polonium...	210	136 days	RaE	α	0.0523	3.58
Radium A..	218	3.05 min.	Rn	α	0.0565	4.50
Thorium A .	216	0.14 sec.	Tn	α	0.060	5.40
Actinium A.	214?	2×10^{-3} sec.	An	α	0.063	6.1
Actinium C′	210?	10^{-3} sec.	AcC(?)	α		6.1
Radium C′ .	214	10^{-7} sec.	RaC	α	0.064	6.57
Thorium C′.	212	10^{-11} sec.	ThC	α	0.069	8.16

Like lead ion, it may be deposited by anodic oxidation as the dioxide:

$$Po^{++} + 2H_2O = PoO_2 + 4H^+ + 2E^-; \quad -1.5 \text{ volts}$$

Polonium is precipitated by hydrogen sulfide, presumably as PoS, and there is evidence for the formation of a very unstable hydride, PoH_2.

Polonium is conveniently prepared from radium D or radio-lead by fractional crystallization of the nitrates, or by the electrolytic reduction of the polonium.

The isotopes of polonium constitute part of the so-called "active deposits" formed by the disintegration of radon and its isotopes. They are usually collected by hanging negatively charged platinum foil in the gas. The extremely unstable C′ elements are notable for their very penetrating alpha particles.

SUBGROUP V, ATOMIC NUMBER 83

	Atomic Weight	Half Period	Parent Element	Radiation	Vel. of Particle Rel. to Light	Range, cm., in Air, 0° and 1 Atm.
Bismuth....	209	Stable				
Radium E..	210	4.85 days	RaD	β		
Thorium C .	212	60.8 min.	ThB	β, α	β .30 to 95	
Radium C..	214	19.5 min.	RaB	β, α	β .78 to 95	
Actinium C.	210?	2.16 min.	AcB	α, (β?)	α0.059	5.12

13. The chemistry of bismuth is considered in Chapter **XVI,** and the chemical properties of its radioactive isotopes are

doubtless the same. These isotopes may be separated from the "active deposit" (Par. 12) by taking advantage of decreasing ease of cathodic reduction from Subgroup VI to Subgroup IV. Simple heating of the active deposit on a platinum foil gives a partial separation, as the lead isotopes are more volatile than those of bismuth.

The "C" elements undergo both β and α decomposition, the percentages of the β changes being RaC, 99.97; AcC, 0.2; ThC, 65.

SUBGROUP IV, ATOMIC NUMBER 82

	Atomic Weight	Half Period	Parent Element	Radiation	Vel. of Particle Rel. to Light
Lead (ordinary)..	207.22	Stable			
Radium G.....	206	"	Po	Rayless	
Thorium D.....	208	"	ThC', ThC''?	Rayless	
Actinium D.....	206?	"	AcC'', AcC'?	Rayless	
Radium D.....	210	16 yrs.	RaC', RaC''?	β	0.33 to 0.39
Thorium B.....	212	10.6 hrs.	ThA	β	0.63 to 0.72
Actinium B.....	210?	36.1 min.	AcA	β	
Radium B.....	214	26.8 "	RaA	β	0.36 to 0.74

14. Most uranium ores contain radium G mixed with ordinary lead, but the mineral curite gives pure radium G with an experimental atomic weight of 206.09, thus agreeing very closely with that predicted from the atomic weight of uranium. The purest thorium D which has been obtained from thorium minerals has an atomic weight of 207.9.

Radium D differs from the other two "D" elements in undergoing further decomposition. It has been isolated from radium preparations in barely visible quantities.

The "B" elements are present in the "active deposit" of the emanations, and may be separated by the greater volatility of their oxides, and by the fact that they are more electropositive than the isotopes of bismuth and polonium.

One g. of uranium in equilibrium with its products gives 1.26×10^{-10} g. of Pb_{206} per year, and 1 g. of thorium 4.8×10^{-11} g. of Pb_{208} per year. These figures are used in estimating the age of various minerals.

Subgroup III, Atomic Number 81

	Atomic Weight	Half Period	Parent Element	Radiation
Thallium	204.39	Stable		
Actinium C″	206?	4.76 min.	AcC	β
Thorium C″	208	3.2 "	ThC	β
Radium C″	210	1.3 "	RaC	β

15. The very unstable isotopes of thallium may be isolated by collecting on a negative foil placed opposite a foil containing "active deposit" (Par. **12**), since they are ejected from the deposit as the "recoil" product of the disintegration of the "C" elements. It is assumed that the product of their β disintegration is the same "D" element as is formed from the "C" elements.

Potassium and Rubidium

16. Potassium and rubidium possess beta activity, the magnitude of the latter being about 1/15 that of uranium. Potassium emits a smaller number of particles, but these are more penetrating, having a velocity 88 per cent of that of light, as compared to 60 per cent for rubidium. It is not known whether this activity arises in the common atomic species, or in isotopes which may be present only in small amounts.

GLOSSARY

Acid.—A substance which gives hydrogen ion in solution, or which neutralizes bases yielding water.

Activity.—Cf. Appendix IV.

Allotropy.—The property shown by certain elements of being capable of existence in more than one form, due to differences in the arrangement of atoms or molecules. (See Monotropic and Enantiotropic.)

Alpha particles.—Doubly charged helium atoms shot off during one type of radioactive change.

Ampere.—Unit of electric current strength; one coulomb per second; the international ampere is the current which deposits 0.0011180 g. of silver per second.

Ångstrom unit.—10^{-10} meters; 10^{-8} cm.

Angular momentum.—Product of the angular velocity and moment of inertia. The latter is analogous to the mass in simple translation. Unit expressed in g. cm^2/sec.

Anhydride (of acid or base).—An oxide which when combined with water gives an acid or base.

Anode.—The electrode at which oxidation occurs.

Atmosphere.—Unit of pressure. Defined as pressure exerted by a column of mercury 76 cm. high; 1.01325×10^6 dynes per cm^2; 14.7 lbs. per sq. inch.

Atom.—The unit particle of an element. A nucleus of definite integral positive charge surrounded by electrons.

Atomic number.—The net positive charge on the nucleus of an atom; the ordinal number of an atom in the periodic system.

Atomic weight.—Weight of an atom referred to the oxygen atom as 16.000.

Avogadro's number.—The number of molecules in a mole; 6.061×10^{23}.

Avogadro's rule.—Equal volumes of all gases, at the same temperature and pressure, contain the same number of molecules (approximately).

Bar.—Unit of pressure; $= 10^6$ dyne cm^2; one atmosphere = 1.013 bar.

Base.—A substance which gives hydroxide ion in solution, or which neutralizes acids yielding water.

Base element.—An easily oxidized element, as opposed to a noble element.

Boiling point.—The temperature at which the vapor pressure of a liquid reaches standard atmospheric pressure.

British thermal unit (BTU).—Heat required to raise 1 lb. of water 1° F.

Calorie.—Unit of energy. Small calorie (denoted by cal.) is heat required to raise 1 g. of water 1° C. Kg. cal. = 1000 cal. Value varies with temperature. 1 cal (15° C.) = 4.185 joules.

Catalyst.—A substance which by its presence alters the rate of a reaction and itself remains unchanged at the end of the reaction.

Cathode.—The electrode at which reduction occurs.

Cathode rays.—A stream of electrons.

Centigrade (C).—Temperature scale in which freezing point of water is called 0° and boiling point 100°.

Chemiluminescence.—Emission of light during a chemical reaction.

Colloid.—A phase dispersed to such a degree that the surface forces become an important factor in determining its properties.

Coloumb.—The quantity of electricity transferred in one second by a current of one ampere; a coulomb can deposit 0.0011180 g. of silver.

Component.—One of the minimum number of substances required to state the composition of all phases of a system.

Concentration.—The amount of a substance in weight, moles, or equivalents contained in unit volume.

Conductance.—Reciprocal of resistance. $C = \overline{C}\ A/L$, where A is cross section L, length, and $\overline{C}$, *specific conductance.*

Coordination number of an atom.—The number of atoms, molecules or radicals which are held about it in relatively stable positions.

Critical pressure.—The pressure exerted by a system at its critical temperature.

Critical temperature.—The highest temperature at which a liquid and its vapor may coexist as distinct phases.

Critical volume.—The volume of unit mass at the critical temperature and pressure.

Curie.—The amount of radon which can exist in a steady state, "equilibrium," with 1 g. of radium.

Decomposition voltage.—Cf. Appendix I.

Degree of freedom.—The number of the variables determining the state of a system (usually pressure, temperature, and concentrations of the components) to which arbitrary values can be assigned.

Degree of ionization.—Cf. Appendix III.

Density (volume-density).—The mass per unit volume: g. per cc.

Diamagnetic.—An object of diamagnetic material will set the longest dimension at a right angle to the magnetic field. When a diamagnetic substance is placed in a magnetic field, the lines of force are spread out. (See Paramagnetic.)

Dielectric constant.—The force between two point charges (e, e′) separated by the distance r in a uniform medium is $f = ee'/kr$ where k is called the dielectric constant.

Diffusion law.—The rates of diffusion of two gases are inversely proportional to the square roots of the densities of the gases.

Distribution Law.—A substance distributes itself between two immiscible solvents so that the ratio of its concentrations in the two solvents is approximately a constant (and equal to the ratio of the solubilities of the substance in each solvent). Requires modification if more than one molecular species is formed.

Dyne.—Unit of force. The force which will impart to a mass of 1 g. an acceleration of 1 cm. per sec.^{2}; 1 g. = 980 dynes.

Elastic limit.—The maximum stress to which a material may be subjected and still return to its original form.

Energy.—Work, or the capacity for doing work.

Electromotive force.—See Potential.

Electron.—The unit charge or atom of negative electricity; 4.774×10^{-10} electrostatic units.

Electropositive element.—An element that is readily oxidized, i. e. forms compounds of positive valence number, syn—base element.

Electron affinity.—The energy of attachment of an additional electron to a neutral atom.

Enantiotropic.—Crystal forms capable of existing in reversible equilibrium with each other.

Entropy.—A measure of the irreversibility of a process; multiplied by the absolute temperature it is the energy required to restore a system which has changed from state A to B to its original state. The property is extensive; for all pure crystals it is zero at the absolute zero.

Equilibrium, chemical.—A state of affairs in which a chemical reaction and its reverse reaction are taking place at equal velocities, so that the concentrations of reacting substances remain constant.

Equivalent (g. equivalent weight).—(1) Acid or base: the amount (weight) of substance necessary to give one mole of hydrogen or hydroxyl, respectively, in a neutralization reaction; (2) oxidizing or reducing agent; a mole of substance divided by the valence change it undergoes in a specified reaction.

Equilibrium constant.—The product of the concentrations (or activities) of the substances produced at equilibrium in a chemical reaction divided by the product of concentrations of the reacting substances, each concentration raised to that power which is the coefficient of the substance in the chemical equation.

Erg.—Work done by a force of 1 dyne acting through a distance of one cm.

Eutectic.—The term applied to a minimum in the freezing point-composition curve of a system.

Fahrenheit.—Temperature scale in which 32° denotes the freezing point and 212° the boiling point of water.

FARAD.—Capacity of a condenser which is charged to a potential of 1 volt by 1 coulomb.

FARADAY.—96,500 coulombs; the charge of 1 mole (6.06×10^{23}) of electrons; the amount of electricity required to precipitate one mole of a singly charged ion.

FLORESCENCE.—The emission of light (other than reflected light) by a substance under illumination.

FLUX.—In metallurgy, a substance which will unite with some of the reaction products to form an easily fusible magma.

FORCE.—That which is capable of imparting acceleration to a mass.

FREE ENERGY.—Cf. Appendix III.

GAS.—A state of matter in which a given mass of a substance has neither definite size nor shape.

GAS CONSTANT.—The constant of the ideal gas equation relating volume, pressure, temperature, and mass (number of moles). $PV = NRT$. $R = 8.315 \times 10^7$ ergs per degree per mole; 0.08206 liter atmos. per degree per mole; 1,9869 cal. (15°) per degree per mole.

GRAM.—A unit of mass (or weight). The mass (approximately) of 1 cc. of water at 4°C.

GRAM ATOM.—A mass in grams numerically equal to the atomic weight.

GRAM MOLECULE.—See Mole. A mass in grams numerically equal to the molecular weight of the substance in question.

HEAT.—A form of energy.

HUMIDITY.—The amount of water vapor per unit volume of gas. *Relative humidity* is the ratio of the actual partial pressure of water vapor to the equilibrium pressure, water (liquid) to water vapor, at the same temperature.

HYDROLYSIS.—A reaction involving the splitting of water into its ions, and the formation of a weak acid or base or both.

ION.—A charged atom or chemical radical.

IONIZATION POTENTIAL.—The potential required to transfer an electron from its normal quantum level to infinity.

ISOMERISM.—Existence of molecules having the same number and kinds of atoms but in different configurations.

ISOTOPES.—The term applied to atomic species having the same atomic number but different nuclear structure, as indicated by different atomic weight or different type of radioactivity.

JOULE.—Unit of energy = 10^7 ergs; work done per second in forcing 1 ampere through a resistance of 1 ohm.

JOULE-THOMSON EFFECT.—The temperature change in a gas when it expands without doing external work.

KELVIN.—Name applied to absolute-centigrade or thermodynamic temperature scale.

KERNEL.—The atomic nucleus plus all of the electrons except those in the valence shell.

KILO.—Prefix denoting 1000.

LATENT HEAT.—The heat absorbed or evolved in an isothermal reversible process such as melting or vaporization.

LATTICE ENERGY.—The energy required to separate the ions of a crystal to an infinite distance from each other.

LITER.—A unit of volume, 1000 cc.

LOSCHMIDT'S NUMBER.—Equivalent to Avogadro's number.

MASS.—Quantity of matter. Determined as the resistance offered by an object to a change of its motion, i.e., inertia.

MASS LAW.—See Equilibrium Constant.

MEGA.—Prefix meaning 1,000,000.

MELTING POINT.—The temperature at which a solid is in equilibrium with its liquid form (varies with pressure).

METAL.—A substance possessing so called metallic properties, i.e. electric conductivity, heat conductivity, high reflectivity, luster, etc., properties due to the high degree of freedom possessed by electrons of the substance.

MICRO.—Prefix denoting 10^{-6}.

MICRON.—(μ) Unit of length = 10^{-6} meters = 10^{-3} mm.

MILLI.—Prefix denoting 10^{-3}.

MHO.—One reciprocal ohm.

MOLE.—The weight of a substance in grams, numerically equal to its molecular weight; a "gram-molecule."

MOLECULAR VOLUME.—Volume occupied by one mole. 22.4115 l. at 0°C and 1 Atm.

MOLECULAR WEIGHT.—The sum of the atomic weights of all the atoms of the molecule.

MOLECULE.—The smallest physical unit of a substance.

MOMENT OF FORCE.—The moment about a point = force $\times$ perpendicular distance from point to line of force.

MOMENT OF INERTIA.—The sum of the products of each element of mass times the square of its distance from its axis of rotation.

MOMENTUM.—The product of mass times velocity.

MONOTROPIC.—Crystal forms one of which is always metastable with respect to the other.

NORMAL SOLUTION.—One having a concentration of 1 equivalent per liter.

OCTET.—The term applied to a group of eight electrons in the outer atomic shell.

OHM.—Unit of electrical resistance. The resistance of a uniform column of mercury at 0° C. which has a mass of 14.4521 g. and a length of 106.300 cm.

OHM-CENTIMETER.—Unit of volume resistivity. A resistance of one ohm across a centimeter cube.

OVERVOLTAGE.—Cf. Appendix I.

OXIDATION.—An increase in the positive valence number of an element; the loss of electrons by an atom or group of atoms.

PARAMAGNETIC.—An object of paramagnetic material will set the

longest dimension parallel to magnetic field, and the lines of magnetic force will converge toward it.

Passive.—The term applied to the condition produced by treating certain metals with powerful oxidizing agents whereby the metal is rendered in effect more electronegative, e.g., iron treated with fuming nitric acid is rendered passive, and in this condition is not oxidized by silver nitrate solution as is non-passive iron.

Phase.—All of the homogeneous regions of a system which are of the same kind.

Phase Rule.—In a system at equilibrium, the number of phases plus the number of degrees of freedom equals the number of components plus two.

Phosphorescence.—Remission of light after previous illumination.

Photoelectric effect.—The emission of electrons under the action of light.

Planck's constant.—The constant relating the energy and frequency of radiation. $E = h\nu$, $h = 6.554 \times 10^{-27}$ erg. sec.

Polarization (electrical).—Refers to a distribution of electrical charges that gives rise to an external electric field.

Polarization (light).—Light is said to be polarized which exhibits different properties in different directions at right angles to the line of propagation.

Polymorphism.—The ability to exist in two or more crystalline forms.

Potential (electric, gravitational, etc., at a point in a field).—The work required to move a unit quantity (electron, gram, etc.) from the standard position, or position of reference, to the point in question.

Power.—The time rate of doing work, e.g., ergs per second.

Pressure.—Normal force per unit area.

Proton.—The unit charge or atom of positive electricity; the nucleus of the hydrogen atom.

Quantum number.—One of the integers defining the energy of an atom.

Radio-activity.—Changes involving the partial disintegration of the atomic nucleus. Cf. Chapter XXII.

Reduction.—The opposite of oxidation; decrease in positive valence number; gain in number of electrons by an atom or group of atoms.

Refractive index.—The ratio of the sine of the angle of incidence of a beam of light from a vacuum upon a substance to the sine of the angle of refraction. $n = \sin i / \sin r$. It is also the ratio of velocity of light in vacuum to that in the medium.

Replacement series.—The arrangement of the metals in order of the values of their oxidation potentials.

Resistance (electrical) R.—Defined as the quotient of the potential E, between two surfaces, divided by the resulting current I,

flowing from one to the other, as defined by Ohm's law, $R = E/I$.

Rydberg's constant.—A fundamental constant appearing in the expression relating the terms of the hydrogen spectrum.

Solubility.—The amount of solute (expressed in grams, moles, etc.) present in a given amount (grams, moles, volume, etc.) of solvent or of solution.

Solubility product.—The equilibrium constant for the solution of a solid strong electrolyte, e.g. for Cu_2S, $K = (Cu^+)^2 \times (S^{--})$.

Solute.—That constituent of a solution which is considered to be dissolved in the other, the solvent. The solvent is usually present in larger amount than the solute.

Solution.—A homogeneous mixture, the proportion of whose constituents may be varied within certain limits. Solutions may be either liquid, solid, or gaseous.

Solvent.—That constituent of a solution which is present in larger amount; or, the constituent which is liquid in the pure state, in the case of solutions of solids or gases in liquids.

Specific gravity.—The ratio of the mass of a certain volume of a substance to the mass of the same volume of a reference substance, generally water, for solids and liquids, and air for gases. The reference substance is at a specified temperature.

Specific heat.—The heat required to raise a unit mass (1 g.) of a substance 1 degree.

Specific volume.—The volume of 1 gram.

Spectrum.—Light resolved into its component frequencies, as by a prism or diffraction grating.

Standard conditions (of a gas).—0° C. and one atmosphere, or 760 mm. pressure.

Standard potential.—Cf. Appendix I.

Stephan's constant.—The constant relating total black body radiation and the absolute temperature. $J = \sigma T^4$. $\sigma = 5.709 \times 10^{-5}$ erg per cm^2 per sec. per deg^4.

Stoichiometric.—Pertaining to weight relations in chemical reactions.

Surface tension.—The contractive force of a surface measured along unit length of its edge, usually expressed in dynes per cm.; this is numerically equal to the work done in extending the surface 1 cm^2., in ergs per cm^2.

System.—An isolated group of substances.

Temperature.—The condition which determines whether heat will flow to or from one body to another. See also Absolute, Centigrade.

Thermoelectric force.—The potential between the junctions of two metal wires which arises when the two junctions are at different temperatures.

Triple point (in one component system).—Temperature and pressure at which three phases are in equilibrium, usually refers to liquid-solid-gas systems.

VALENCE.—Used as the polar valence number, it is the excess of positive or negative charge on the atom or radical. Non-polar valence is the number of atoms attached to a given atom, and probably can be interpreted as meaning the number of electron pairs shared with other atoms. See also Coordination Number.

VAN DER WAALS' EQUATION.—An equation relating the volume, pressure, and temperature of an imperfect gas in terms of two emperical constants. $(P + a/v^2)(v - b) = RT$.

VISCOSITY.—The internal friction of a fluid; the reciprocal of fluidity.

VOLT.—The potential difference required to produce a current of one ampere through a resistance of one ohm.

WATT.—Unit of power, work performed at the rate of one joule per second.

WAVE LENGTH (of light).—Distance between consecutive corresponding points in the light wave. Expressed in units of length, Ängstrom, microns, etc. Sodium yellow line = 5890 Ä = 589 $\times 10^{-6}$ mm. = 0.589 μ.

X-RAYS.—High frequency light waves originating from the electrons of the kernel.

APPENDIX I

SUMMARY OF FUNDAMENTAL CONCEPTS RELATING TO ELECTROLYTIC OXIDATION AND REDUCTION

(1) An electric current is carried through a solution of an electrolyte by the motion of its ions; the positive ions moving toward the cathode and the negative ions toward the anode. The current carried by each species of ion is proportional to its concentration and velocity.

(2) Electricity is transferred from the electrolyte to the electrodes through the mechanism of electrode reactions, also called "half reactions," which always involve the liberation of electrons at the anode and the using up of electrons at the cathode. The substances entering into either electrode reaction may be positive ions, negative ions, or neutral molecules.

(3) The sum of the two electrode reactions is the cell reaction. If this reaction takes place spontaneously, we have a **battery** or **electric cell** capable of doing external work. If this reaction is not spontaneous, an external electromotive force must be used to force electricity through the cell and the process is called **electrolysis.**

(4) **Faraday Laws.**—The extent of the electrode reactions is proportional to the total current that passes, and the passage of one Faraday (96500 coulombs) of electricity causes the electrode reaction to proceed to such an extent that one equivalent of each substance involved in the cell reaction is used up or produced.

(5) At the cathode that reduction process occurs which has the highest oxidation potential; and at the anode that oxidation process occurs which has the highest reduction potential, with the exception that the speed of a given electrode reaction may be so slow that a reaction requiring a larger amount of free energy may take place first. Use may be made of a table of oxidation-reduction potentials, Appendix II, in order to predict the reaction that should theoretically take place at each electrode.

The potential of the cell reaction is the difference in potential of the two half reactions, e.g.

$Zn = Zn^{++} + 2E^{-}$	0.758 volts
$2Ag = 2Ag^{+} + 2E^{-}$	− 0.799 volts
$Zn + 2Ag^{+} = Zn^{++} + 2Ag$	1.55 volts

(6) The standard potential values are based upon measurements with very small currents. In general, if a solution is being electrolyzed with appreciable current, the potential required is greater than the reversible electrode potentials, due to irreversible changes taking place.

$$E_{electrolysis} = E_{0\ (reversible)} + E_{irreversible}$$

The irreversible potential required is known as **overvoltage** and may be traced to two general causes:

First. The potential necessary to overcome the resistance of the solution. If a large current is flowing, the resistance of the electrolyte may increase very markedly, due to the rapidity with which the ions are being used up in the immediate vicinity of the electrodes. This effect is sometimes known as **concentration polarization.**

Second. Many of the electrode reactions are slow, and in order to get them to go with the speed required by large currents, additional potential or driving force must be used. This is especially true of gas reactions. These overvoltages depend not only upon the current density but also upon the nature of the electrode, as is indicated by the experimental results given in Table I. Overvoltage decreases with increasing temperature.

TABLE I

OVERVOLTAGES, IN VOLTS, OF HYDROGEN, OXYGEN, AND CHLORINE AT 25° C.

CURRENT DENSITIES IN AMPERES PER CM.^{2}.

Nature of Electrode	H_2 in 1 *M* H_2SO_4				H_2 in 1 *M* NaOH	O_2 in 1 *M* NaOH			O_2 in 1 *M* H_2SO_4	Cl_2 in NaCl	
	Current Density				Current Density	Current Density			Current Density	Current Density	
	0.001	0.01	0.1	1.0	0.01	0.01	0.1	1.0	0.1	0.01	0.1
Pt (smooth)		0.07	0.28	0.68	0.54	0.85	1.28	1.49	0.4	0.03	0.05
Pt (black)	0.003	0.03	0.04	0.05		0.52	0.64	0.77		0.02	0.03
Au	0.12	0.39	0.59	0.80		0.96	1.24	1.63			
Cu	0.35	0.58	0.80	1.25	0.91	0.58	0.66	0.79			
Ag	0.30	0.76	0.87	1.08	0.61	0.73	0.98	1.13			
Al	0.50	0.83	1.00	1.29							
Sn	0.40	1.08	1.22	1.23	0.94						
Zn		0.75	1.06	1.23	1.05						
Pb		1.09	1.18	1.26							
Fe	0.22	0.56	0.81	1.29	0.54	0.55					
Hg	0.6	1.04	1.06	1.12							
C (graphite)	0.31	0.78	0.98	1.22		0.90	1.09	1.24			0.25

TABLE II

OVERVOLTAGES OF METAL IONS, VOLTS

Electrode	Current Density, I/cm.^{2}		
	0.0001	0.002	0.1
Fe in Fe^{++}	0.129	0.141	0.3
Cu in Cu^{++}	0.011	0.013	0.02
Ag in Ag^{+}			0.00
Zn in Zn^{++}			0.02
Ni in Ni^{++}			0.8

APPENDIX II

STANDARD OXIDATION-REDUCTION POTENTIALS

VALUES, IN VOLTS, REFERRED TO THE HYDROGEN-HYDROGEN ION COUPLE AS ZERO, ARE FOR UNIT ACTIVITIES AND TEMPERATURE OF 25° C.

(Cf. notes at end of table)

Reaction		E_0
$Li = Li^+ + E^-$		+ 2.957
$Rb = Rb^+ + E^-$		+ 2.924
$K = K^+ + E^-$		+ 2.922
$Sr = Sr^{++} + 2E^-$		+ 2.92
$Ba = Ba^{++} + 2E^-$		+ 2.90
$Ca = Ca^{++} + 2E$		+ 2.87
$Na = Na^+ + E^-$		+ 2.712
$Mg = Mg^{++} + 2E^-$		+ 2.40
$Al = Al^{+++} + 3E^-$		+ 1.7
$Be = Be^{++} + 2E^-$		+ 1.69
$U = U^{+4} + 4E^-$		+ 1.4
$Mn = Mn^{++} + 2E^-$		+ 1.1
$CN^- + 2OH^- = CNO^- + H_2O + 2E^-$		+ 0.97
$Fe + 2OH^- = Fe(OH)_2 + 2E^-$		+ 0.86
$\frac{1}{2}H_2 + OH^- = H_2O + E^-$		+ 0.828
$Tl + I^- = TlI + E^-$		+ 0.77
$Hg + HS^- + OH^- = HgS + H_2O + 2E^-$		+ 0.77
$Zn = Zn^{++} + 2E^-$		+ 0.758
$Zn + 3OH^- = HZnO_2^- + H_2O + 2E^-$		+ 0.72
$H_2Te = Te + 2H^+ + 2E^-$	ca	+ 0.7
$Fe(OH)_2 + OH^- = Fe(OH)_3 + E^-$		+ 0.65
$Cr = Cr^{++} + 2E^-$		+ 0.6
$Pb + 2OH^- = PbO + H_2O + 2E^-$		+ 0.58
$S^{--} = S + 2E^-$		+ 0.51
$H_2Se = Se + 2H^+ + 2E^-$	ca	+ 0.5
$Ga = Ga^{+++} + 3E^-$		+ 0.5
$Ag + 2CN^- = Ag(CN)_2^- + E^-$		+ 0.5
$Fe = Fe^{++} + 2E^-$		+ 0.44
$Cr^{++} = Cr^{+++} + E^-$		+ 0.4
$H_2 = 2H^+(10^{-7}\ M) + 2E^-$		+ 0.414
$Cd = Cd^{++} + 2E^-$		+ 0.397
$In = In^{+++} + 3E^-$		+ 0.38
$Ti^{++} = Ti^{+++} + E^-$		+ 0.37
$2Cu + 2OH^- = Cu_2O + H_2O + 2E^-$		+ 0.34
$Tl = Tl^+ + E^-$		+ 0.336
$Pb + SO_4^{--} = PbSO_4 + 2E^-$		+ 0.31
$P + 4H_2O = H_3PO_4 + 5H^+ + 5E^-$		+ 0.3
$Co(CN)_6^{----} = Co(CN)_6^{---} + E^-$		+ 0.3
$Co = Co^{++} + 2E^-$		+ 0.29
$Ni = Ni^{++} + 2E^-$		+ 0.22
$V^{++} = V^{+++} + E^-$		+ 0.2
$Cu + I^- = CuI + E^-$		+ 0.17
$Ag + I^- = AgI + E^-$		+ 0.15
$Cu_2O + 2OH^- = 2CuO + H_2O + 2E^-$		+ 0.15
$Sn = Sn^{++} + 2E^-$		+ 0.13
$Pb = Pb^{++} + 2E^-$		+ 0.12
$9OH^- + NH_3 = NO_3^- + 6H_2O + 8E^-$		+ 0.12
$2Hg + 2I^- = Hg_2I_2 + 2E^-$		+ 0.04
$2Ag + H_2S = Ag_2S + 2H^+ + 2E^-$		+ 0.036
$Cu + H_2S = CuS + 2H^+ + 2E^-$		+ 0.02
$H_2 = 2H^+ + 2E^-$		0.000
$2OH^- + NO_2^- = NO_3^- + H_2O + 2E^-$		0.0
$HCN + H_2O = HCNO + 2H^+ + 2E^-$		0.0
$Sb + 3H_2O = H_3SbO_3 + 3H^+ + 3E^-$	ca	0.0
$W + 3H_2O = WO_3 + 6H^+ + 6E^-$	ca	0.0
$WO^{+++} + 2H_2O = WO_3 + 4H^+ + E^-$	ca	0.0
$Ti^{+++} + H_2O = TiO^{++} + 2H^+ + E^-$		− 0.04
$Hg + 2OH^- = HgO + H_2O + 2E^-$		− 0.099
$Ag + Br^- = AgBr + E^-$		− 0.10
$2Hg + 2Br^- = Hg_2Br_2 + 2E^-$		− 0.13
$Sn^{++} = Sn^{++++} + 2E^-$		− 0.13
$H_2O + H_2SO_3 = SO_4^{--} + 4H^+ + 2E^-$		− 0.14
$Cu^+ = Cu^{++} + E^-$		− 0.17
$H_2S = S + 2H^+ + 2E^-$		− 0.17
$Bi = Bi^{+++} + 3E^-$		− 0.2
$2Ta + 5H_2O = Ta_2O_5 + 10H^+ + 10E^-$	ca	− 0.2
$Pt + 4Cl^- = PtCl_4^{--} + 2E^-$	ca	− 0.2
$Ag + Cl^- = AgCl + E^-$		− 0.223
$As + 3H_2O = H_3AsO_3 + 3H^+ + 3E^-$		− 0.24
$Mo + 3H_2O = MoO_3 + 6H^+ + 6E^-$		− 0.25
$2Hg + 2Cl^- = Hg_2Cl_2 + 2E^-$		− 0.270
$PbO + 2OH^- = PbO_2 + H_2O + 2E^-$		− 0.3
$V + H_2O = VO^{++} + 2H^+ + 4E^-$		− 0.3
$Cu = Cu^{++} + 2E^-$		− 0.344
$V^{+++} + H_2O = VO^{++} + 2H^+ + E^-$		− 0.4
$4OH^- = O_2 + 2H_2O + 4E^-$		− 0.40
$PtCl_4^{--} + 2Cl^- = PtCl_6^{--} + 2E^-$	ca	− 0.40
$U^{+4} + 2H_2O = UO_2^{++} + 4H^+ + 2E^-$		− 0.41
$S + 3H_2O = H_2SO_3 + 4H^+ + 4E^-$		− 0.47
$Fe(CN)_6^{----} = Fe(CN)_6^{---} + E^-$		− 0.49
$H_3AsO_3 + H_2O = H_3AsO_4 + 2H^+ + 2E^-$		− 0.49
$Ni(OH)_2 + 2OH^- = NiO_2 \cdot 2H_2O + 2E^-$		− 0.49
$2Ag + CO_3^{--} = Ag_2CO_3 + 2E^-$		− 0.50
$MoO^{+++} + 2H_2O = MoO_3 + 4H^+ + E^-$		− 0.5
$Cu = Cu^+ + E^-$		− 0.51
$2I^- = I_2 + 2E^-$		− 0.535
$3I^- = I_3^- + 2E^-$		− 0.54
$Hg_2Cl_2 + 2Cl^- = 2HgCl_2 + 2E^-$		− 0.63
$MnO_4^{--} = MnO_4^- + E^-$		− 0.66
$H_2O_2 = O_2 + 2H^+ + 2E^-$		− 0.68

Reaction	E_0	Reaction	E_0
$Ag + BrO_3^- = AgBrO_3 + E^-$	− 0.68	$Cr^{+++} + 4H_2O = HCrO_4^- + 7H^+ + 3E^-$	− 1.3
$C_6H_4(OH)_2 = C_6H_4O_2$ (quinone) $+ 2H^+ + 2E^-$	− 0.70	$Br^- + H_2O = HBrO + H^+ + 2E^-$	− 1.33
$MnO_2 + 4OH^- = MnO_4^{--} + 2H_2O + 2E^-$	− 0.71	$Mn^{++} + 2H_2O = MnO_2 + 4H^+ + 2E^-$	− 1.33
$Fe^{++} = Fe^{+++} + E^-$	− 0.74	$Cl^- + 4H_2O = ClO_4^- + 8H^+ + 8E^-$	− 1.35
$Se + 3H_2O = H_2SeO_3 + 4H^+ + 4E^-$	− 0.74	$2Cl^- = Cl_2 + 2E^-$	− 1.359
$H_3SbO_3 + H_2O = H_3SbO_4 + 2H^+ + 2E^-$	− 0.75	$2Au + 3H_2O = Au_2O_3 + 6H^+ + 6E^-$	1.362
$2Hg = Hg_2^{++} + 2E^-$	− 0.798	$I^- + 4H_2O = IO_4^- + 8H^+ + 8E^-$	− 1.4
$Ag = Ag^+ + E^-$	− 0.799	$Br^- + 3H_2O = BrO_3^- + 6H^+ + 6E^-$	− 1.42
$CuI = Cu^{++} + I^- + E^-$	− 0.85	$Pb^{++} + 2H_2O = PbO_2 + 4H^+ + 2E^-$	− 1.44
$Hg = Hg^{++} + 2E^-$	− 0.86	$Cl^- + 3H_2O = ClO_3^- + 6H^+ + 6E^-$	− 1.45
$2H_2O + NH_4^+ = HNO_2 + 7H^+ + 6E^-$	− 0.86	$Cl^- + H_2O = HClO + H^+ + 2E^-$	− 1.50
$3OH^- = HO_2^- + H_2O + 2E^-$	− 0.87	$Mn^{++} = Mn^{+++} + E^-$	ca − 1.5
$CoO + 2OH^- = CoO_2 + H_2O + 2E^-$	− 0.9	$Au = Au^+ + E^-$	ca − 1.5
$Hg_2^{++} = 2Hg^{++} + 2E^-$	− 0.92	$2SO_4^{--} + 2H^+ = H_2S_2O_8 + 2E^-$	ca − 1.5
$Cl^- + 2OH^- = ClO^- + H_2O + 2E^-$	− 0.94	$Ce^{+++} + 2H_2O = CeO_2 + 4H^+ + E^-$	− 1.5
$NO + 2H_2O = NO_3^- + 4H^+ + 3E^-$	− 0.94	$Mn^{++} + 4H_2O = MnO_4^- + 8H^+ + 5E^-$	− 1.52
$HNO_2 + H_2O = NO_3^- + 3H^+ + 2E^-$	− 0.95	$MnO_2 + 2H_2O = MnO_4^- + 4H^+ + 3E^-$	− 1.63
$NO + H_2O = HNO_2 + H^+ + E^-$	− 0.98	$Fe^{+++} + 4H_2O = FeO_4^{--} + 8H^+ + 3E^-$	ca − 1.7
$I^- + H_2O = HIO + H^+ + 2E^-$	− 0.99	$Bi^{+++} + 6H_2O = HBiO_3 + 5H^+ + 2E^-$	ca − 1.7
$OsO_2Cl_4^{--} + 2H_2O = OsO_4 + 4H^+ + 4Cl^- + 2E^-$	ca − 1.0	$PbSO_4 + 2H_2O = PbO_2 + 4H^+ + SO_4^{--} + 2E^-$	− 1.7
$2Br^- = Br_2 + 2E^-$	− 1.065	$2H_2O = H_2O_2 + 2H^+ + 2E^-$	− 1.78
$I^- + 3H_2O = IO_3^- + 6H^+ + 6E^-$	− 1.09	$Co^{++} = Co^{+++} + E^-$	− 1.8
$VO^{++} + 2H_2O = HVO_3 + 3H^+ + E^-$	− 1.1	$Ni^{++} + 4H_2O = NiO_2 \cdot 2H_2O + 4H^+ + 2E^-$	− 1.8
$Tl^+ = Tl^{+++} + 2E^-$	− 1.2	$O_3 + H_2O = O_3 + 2H^+ + 2E^-$	− 1.9
$H_2SeO_3 + H_2O = H_2SeO_4 + 2H^+ + 2E^-$	ca − 1.2	$2F^- = F_2 + 2E^-$	− 2.8
$2H_2O = O_2 + 4H^+ + 4E^-$	− 1.23		
$PdCl_4^{--} + 2Cl^- = PdCl_6^{--} + 2E^-$	− 1.3		

Notes on the Use of the Table of Oxidation-Reduction Potentials

The above table of important oxidation-reduction potentials has been prepared for ready reference. Additional values for couples less frequently employed will be found under the various elements.

The couples are arranged in order of increasing oxidizing power, that is, the oxidized form of any couple has sufficient energy to oxidize the reduced form of any couple of higher positive potential.

The values, which are referred to the potential of the hydrogen-hydrogen ion couple as zero, are for 25° C. and all gas pressures, 1 atmosphere, and all activities (Append. IV), 1 molal unless, otherwise stated.

The potential at other concentrations and pressures at 25° C. is given by the expression:

$$E = E_0 - \frac{0.059}{n} \log Q,$$

where Q is the product of the activities (solutes in moles per liter and gases in atmospheres) of the products divided by the product of the activities of the reacting substances, each activity raised to that power whose exponent is the coefficient of the substance in the half reaction, and n is the number of moles of electrons involved in the half reaction as written. Activities of pure solids and liquids are taken as unity.

Example:

$$2Cl^-(1M) = Cl_2(1 \text{ atm.}) + 2E^-; \quad E_0 = -1.359$$

$$2Cl^-(0.01M) = Cl_2(5 \text{ atm.}) + 2E^-; \quad E = E_0 - \frac{0.059}{2}\log\frac{5}{(0.01)^2}$$

$$E = -1.359 - 0.138 = -1.497$$

These potential values merely represent the difference in energies of the products and the reacting substances and as such give no information as to the speed of the reaction; indeed the mechanism of the reaction may be such that it cannot take place in spite of a favorable potential value. Thus, $Fe = Fe^{+++} + 3E^-$; + 0.04 volts, indicates that H^+ would oxidize iron to the ferric state, but the mechanism of the reaction is $Fe = Fe^{++} + 2E^-$, + 0.44 volts, and $Fe^{++} = Fe^{+++}$, − 0.74 volts, and H^+ cannot bring about the second step.

In general it may be stated that many of the reactions given are not capable of experimental attainment under equilibrium conditions for one of two reasons: (1) the reaction is slow, as, for example, the reduction of sulfuric acid to sulfurous acid in dilute solutions, or the evolution of hydrogen on zinc which may require an overvoltage of 1.2 volts; or (2) the final and initial substances cannot exist together because of an intermediate state, as for example, the $Fe - Fe^{+++}$ couple which gives Fe^{++}, or $Cl^- + H_2O = HClO + H^+ + 2E^-$, which would give Cl_2 at 1 M H^+.

Two half reactions may be added or subtracted to give a third half reaction but the potential of the third reaction is derived by the *addition or subtraction of the free energies* (Append. III) and not by the addition of the potential values. However, if two half reactions are subtracted to give a complete reaction, the potential of the reaction is the *difference in the potentials of the two couples.*

APPENDIX III

FREE ENERGY VALUES AND THEIR USE

Summary of concepts relating to free energy data, and their use in predicting the direction and extent to which a given reaction will proceed:

(1) The free energy of a process is the maximum available work which is obtainable in going from the initial to the final state. The free energy change, ΔF, of a chemical reaction is the free energies of formation (from their elements) of the products of the reaction, less the free energy of formation of the reacting substances. Example: $CaO + 2HCl = CaCl_2 + H_2O$; $\Delta F = F_{CaCl_2} + F_{H_2O} - F_{CaO} - 2F_{HCl}$.

(2) The free energy values for the substances in Table I refer to energy of formation from the elements at 25° in their standard states or states of unit activity, which are pure solid, pure liquid, gas at one atmosphere, and solute at 1 molal activity. The free energy of a reaction, in which all the substances are at unit activity and at temperature T, is designated as ΔF°_T. The free energies of all elements and of H^+ are taken as zero in their standard states.

(3) The relation between the free energy change for substances in their standard states and the equilibrium constant, K, is

$$-RT\ ln_e K = \Delta F^\circ_T, \quad \text{or} \quad -1365 \log_{10} K = \Delta F^\circ_{298^\circ K} \text{ (in cal.)}$$

where R is the gas constant and T the absolute temperature. The more general relation is:

$$-RTlnK/Q = \Delta F_T$$

where Q has the same form as the equilibrium constant but the concentrations refer to the values of the substances in their initial and final states. If these are unity, then Q is unity and the free energy is ΔF°.

Example: We may calculate the equilibrium constant for the reaction: $Cl_{2(aq.)} + H_2O_{(liq.)} = H^+ + Cl^- + HClO_{(sol.)}$, from the value $\Delta F^\circ_{298} = 4525$. Hence $-\log_{10} K = 4525/1365$; $K = (H^+)(Cl^-)(HClO)/(Cl_2) = 4.84 \times 10^{-4}$.

(4) It follows from this relation that a large negative value for ΔF means a large value for K or that the reaction as written is capable of proceeding to practical completion. It must be emphasized again, however, that free energies give no information as to the speed of the reaction.

(5) The reversible electromotive force, E, is a direct measure of the maximum available work or free energy of a chemical reaction:

TABLE OF STANDARD FREE ENERGIES OF FORMATION AT 25° C.

From publications of G. N. Lewis, M. Randall, and Collaborators*

Substance	ΔF°	Substance	ΔF°
All elements in standard state	0	I_3^-	− 12315
NaCl	− 91792	HIO(aq)	− 23170
$KClO_3$	− 69250	IO_3^-	− 31580
AgCl	− 26187		
Ag_2O	− 2395	S(monoc.)	18
Hg_2Cl_2	− 50274	H_2S(g)	− 7840
HgO	− 13808	HsS(aq)	− 6490
$PbCl_2$	− 74990	HS^-	2980
PbO	− 41000	S^{--}	23450
		SO_2(g)	− 69660
		H_2SO_3(aq)	− 126330
O_3(g)	32400	HSO_3^-	− 123920
H_2O(g)	− 54507	SO_3^{--}	− 116680
H_2O(l)	− 56560	SO_3(g)	− 85890
H_2O(s)	− 56418	H_2SO_4(aq)	− 176500
H^+	0	SO_4^{--}	176500
OH^-	− 37455		
H_2O_2(l)	− 28230	NH_3(g)	− 3910
H_2O_2(aq)	− 31470	NH_4OH(aq)	− 62860
HO_2^-	− 15610	NH_4^+	− 18930
		NO(g)	20850
Cl_2(aq)	1650	NO_2(g)	11920
HCl(g)	− 22692	N_2O_4(g)	22640
HCl(aq)	− 31367	HNO_3(aq)	− 13070
Cl^-	− 31367	NO_2^-	− 8500
HClO(aq)	− 19018	HNO_3(aq)	− 26500
ClO^-	− 6500	NO_3^-	− 26500
ClO_3^-	− 250		
ClO_4^-	− 9000	C (diamond)	390
		CH_4(g)	− 12800
Br_2(aq)	− 977	CO(g)	− 32510
HBr(g)	− 12540	CO_2(g)	− 94260
HBr(aq)	− 24595	H_2CO_3(aq)	− 148810
Br^-	− 24595	HCO_3^-	− 140000
Br_3^-	− 25230	CO_3^{--}	− 125670
HBrO(aq)	− 19680	C_2H_5OH(l)	− 45100
BrO_3^-	2300	HCN(aq)	27520
		CN^-	39370
I_2(aq)	3926	HCNO(aq)	− 29100
HI(aq)	315	CNO^-	− 23750
HI(aq)	− 12361	C_2N_2(g)	92000
I^-	− 12361		

* Values for many positive ions which may be calculated directly from the oxidation-reduction potentials have not been included, cf. Ag^+, P.(5) above.

$n \cdot 23060$. $E = -\Delta F$ where n is the number of Faradays of electricity which flow through the circuit, and ΔF is given in calories.

Example: $Ag^+ + \frac{1}{2}H_2 = H^+ + Ag$; $E_0 = 0.799$.

$$\Delta F^\circ = -0.799 \times 23060 = -18440 \text{ cal.}$$

Since the free energies of H_2, H^+, and Ag are zero by definition, F°_{298} of Ag^+ is 18440.

Example: To calculate the solubility product of AgCl at 25° C.

$Ag + Cl^- = AgCl + E^-$	-0.223 volts
$Ag = Ag^+ + E^-$	-0.799 "
$Ag^+ + Cl^- = AgCl$	0.576 volts

Hence $\Delta F^\circ = -0.576 \times 23060 = -1365 \log 1/K$, and $K = 1.06 \times 10^{-10}$.

APPENDIX IV

IONIZATION OF STRONG ELECTROLYTES

The freezing point lowering of a molal solution of a strong electrolyte such as sodium chloride is somewhat less than twice the molal freezing point lowering (cf. Hildebrand, *Princ. of Chem.*, p. 61) and the assumption was formerly made that the sodium chloride was only partially ionized. It is now believed that the sodium chloride is completely ionized in the sense that the ions are capable of independent motion, and that the apparent non-ionization is due to the forces acting

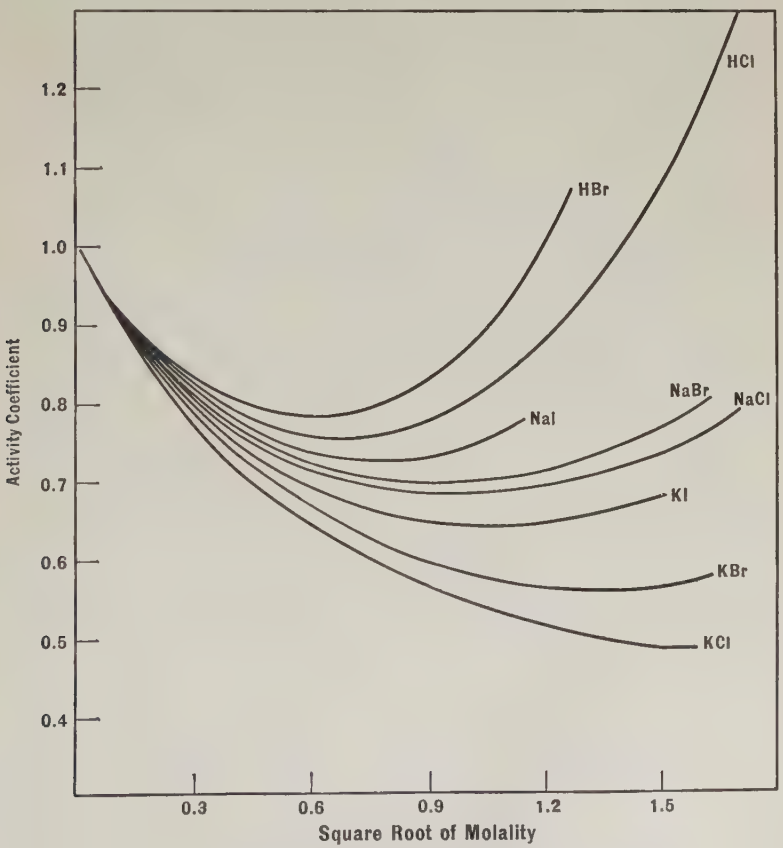


FIG. 1. Activity coefficient of hydrogen and alkali halides.

between an ion and its neighbors in general rather than its attachment to any particular ion. Since this force causes a departure of the ions from the behavior of perfect solutions, it is necessary to use a corrected concentration, called **activity,** a, in all thermodynamic relations, and the ratio of the activity to the concentration (molality) is defined as the **activity coefficient,** $\gamma = a/c$. At infinite dilution the force between the ions is zero and the activity equals the concentration, i.e. $\gamma = 1$ (Fig. 1). As the concentration increases, the activity coefficient becomes less than unity due to the attraction of the oppositely charged ions (Debye and Hückel theory), but at high concentrations other factors enter such as the force of repulsion between the large hydrated ions, or the change in hydration of the ions, and the coefficient may become greater than unity.

It is not possible to measure the activity of an ion of one sign independent of the ion of opposite sign, i.e. Na^+ is not independent of Cl^- in NaCl; hence the activity is determined as the mean of both ions, and the activity coefficient expressed as the mean activity divided by the mean molality. The mean activity and molality are defined in such a manner (cf. Lewis and Randall, *Thermodynamics*, p. 328) that the ratio approaches unity at infinite dilution for all types of salts.

TABLE I

Activity Coefficient of Typical Electrolytes at 25° C.

Molality	0.01	0.05	0.10	1.0
KOH	0.92	0.84	0.80	0.75
HNO_3	0.91	0.83	0.76	
$AgNO_3$	0.90	0.78	0.72	0.39
KIO_3	0.88	0.76	0.69	
$BaCl_2$	0.72	0.57	0.50	
$CdCl_2$	0.53	0.30	0.22	
K_2SO_4	0.69	0.50	0.42	
H_2SO_4	0.62	0.40	0.31	0.15
$MgSO_4$	0.40	0.22	0.17	
$CuSO_4$	0.40	0.22	0.16	
$La(NO_3)_3$	0.57	0.39	0.33	

APPENDIX V

CRYSTAL FORMS AND TYPES OF CRYSTAL LATTICE

A crystal is classified according to the **elements of symmetry** which it possesses. Symmetry is determined by the following operations required to bring the crystal into coincidence with its original position.

(a) **Rotation about an axis.**—If a crystal can be revolved about an axis through its center so that similar faces recur n times in one rotation, it is said to possess n fold symmetry about this axis. Only axes of two-, three-, four-, and six-fold symmetry are known or in fact are possible with a system of particles at finite distances apart.

(b) **Reflection in a Plane.**—A crystal which may be divided by a plane into two parts, mirror images of each other, is said to possess symmetry about this plane.

(c) **Inversion about the Center.**—If every line drawn through the center cuts similar parallel faces on opposite sides of the center, the crystal is said to possess a center of symmetry.

(d) **Simultaneous Rotation and Reflection.**—If a crystal can be revolved about an axis so that n times in one rotation faces recur which are alternate mirror images, the crystal is said to possess an axis of composite symmetry. Only four- and six-fold axes of composite symmetry can occur.

Crystal Classes.—There are 31 possible combinations of these four types of symmetry and these, together with the crystal without any symmetry, constitute the 32 crystal types.

The 32 types are grouped into six **crystal systems** with the following characteristics:

(1) **Isometric or Cubic.**—This system includes all crystals having three interchangeable axes at right angles. All crystals have 4 axes of three-fold symmetry. One of the most important forms is the cube which has 3 axes of four-fold symmetry, 4 axes of three-fold symmetry which also have six-fold composite symmetry, 6 axes of two-fold symmetry, nine planes of symmetry and a center of symmetry. Other forms are the octahedron, dodecahedron, and tetrahedron.

(2) **Tetragonal.**—One four-fold axis (may be four-fold composite axis) and two interchangeable axes at right angles to the principal axis and to each other. The tetragonal prism is a common form.

(3) **Hexagonal.**—One three-fold or six-fold axis of symmetry. Three interchangeable lateral axes of reference are generally employed which are perpendicular to the axes of symmetry and intersect each other at 120°. Hexagonal prisms, hexagonal bipyramids, and rhombohedra are common forms.

Figures of the Simpler Types of Crystal Lattices

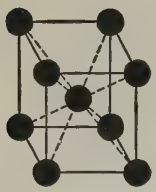


Fig. 1. Body-centered cubic. Structure of Cr, Fe (alpha); Li, Na, K, Mo, Ta, V, W.

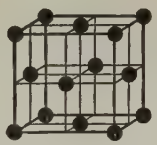


Fig. 2. Face-centered cubic. Structure of Ag, Al, Au, Ca, Ce, Co (cubic), Cu, Fe (beta), Ir, Ni, Pb, Pt, Th and A.

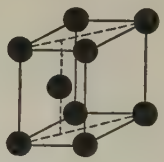


Fig. 3. Hexagonal close-packed. Structure of Be, Cd, Ce, Co, Hf, Mg, Os, Ti, Tl, Zn, Zr.

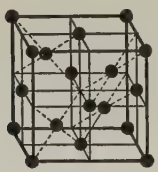


Fig. 4. Diamond type. Structure of C (diamond), Si and Sn (grey).

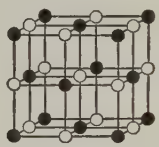


Fig. 5. Sodium chloride type. Structure of lithium, sodium and potassium halides: CaO, SiO, MgS, VN, NiO, CoO, FeO, AgCl, AgBr, PbS, MgO, CoF.

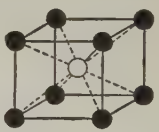


Fig. 6. Cesium chloride type. Structure of CsCl, CsBr, CsI, TlCl, TlBr, TlI.

Fig. 7. Zinc oxide type. Structure of ZnO, AgI, TaN, AlN, BeO.

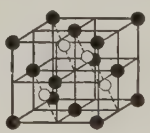


Fig. 8. Zinc sulfide type. Structure of ZnS, HgS, CuCl, CuBr, CuI, AgI.

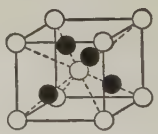


Fig. 9. Cuprous oxide type. Structure of Cu_2O, Ag_2O.

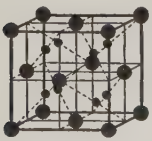


Fig. 10. Calcium fluoride type. Structure of CaF_2, Li_2S, Li_2O, Cu_2Se, Na_2S, BaF_2, PbF_2, SrF_2, HgF_2, ThO_2, CdF_2, CeO_2, UO_2, PrO_2, $SrCl_2$. Ratio of radius of M to radius of X > 0.6.

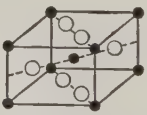


Fig. 11. Rutile type. Structure of TiO_2, PbO_2, MnF_2, TeO_2, FeF_2, ZnF_2, CoF_2, NiF_2, SnO_2, MgF_2, NbO_2, MoO_2, WO_2, IrO_2, VO_2, MnO_2. Ratio of radius of M to radius of X < 0.6.

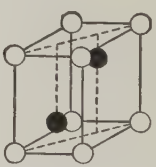


Fig. 12. Manganous hydroxide type. Structure of $Mn(OH)_2$, ZrS_2, CdI_2, $Mg(OH)_2$, $Ca(OH)_2$.

This system is often divided so as to give a **Rhombohedral class,** crystals of which may be referred to 3 axes, all equal and all inclined unequally.

(4) **Orthorhombic.**—Crystals with three non-interchangeable axes of symmetry at right angles to each other. The rhombic prism and rhombic pyramid are common forms.

(5) **Monoclinic.**—Crystal with a single axis of symmetry but not three-, four- or six-fold. Two additional axes of reference are chosen at right angles to the axis of symmetry and usually oblique to each other. A rhombic prism having a two-fold axis, a plane and a center of symmetry is a common form.

(6) **Triclinic.**—Crystal possesses no direction of symmetry. Reference axes are non-interchangeable and in general at oblique angles. Two classes, with and without center of symmetry.

APPENDIX VI

QUALITATIVE ANALYSIS SCHEME

(From A. A. Noyes' *Qualitative Chemical Analysis*)

Basic Constituents

Separation of the Basic Constituents into Groups

Solution in dilute nitric acid containing all the common basic constituents. Add NH_4Cl.

Precipitate: Silver-Group (Bi, Pb, Ag, Hg) as chlorides.	Filtrate: Saturate with H_2S gas.				
	Precipitate: Copper-Group and Tin-Group as sulphides. Treat with $(NH_4)_2S_4$.		Filtrate: Add NH_4OH and $(NH_4)_2S$.		
	Residue: Copper-Group (Hg, Pb, Bi, Cu, Cd), as sulphides.	Solution: (Tin-Group As, Sb, Sn), as ammonium sulpho-salts.	Precipitate: Aluminum-Group and Iron-Group, as hydroxides and sulphides. Dissolve in acid, add NaOH and Na_2O_2.		Filtrate: Add $(NH_4)_2CO_3$.
			Filtrate: Aluminum-Group (Al, Cr, Zn), as sodium salts.	Precipitate: Iron-Group (Mn, Fe, Co, Ni), as hydroxides.	Precipitate: Alkaline-Earth Group (Ba, Sr, Ca, Mg), as carbonates.	Filtrate: Alkali-Group (NH_4, K, Na), as nitrates and chlorides.

Analysis of the Silver Group

Precipitate: $BiOCl$, $PbCl_2$, $AgCl$, Hg_2Cl_2. Treat with HCl.

Solution $BiCl_3$. Evaporate, pour into water.	Residue: $PbCl_2$, $AgCl$, Hg_2Cl_2. Treat with hot water.		
	Solution: $PbCl_2$. Add H_2SO_4.	Residue: $AgCl$, Hg_2Cl_2. Pour NH_4OH through the filter.	
Precipitate: $BiOCl$.	Precipitate: $PbSO_4$.	Black residue: Hg and NH_2HgCl.	Solution: $(NH_3)_2AgCl$. Add HNO_3
			White precipitate: $AgCl$.

Separation of the Copper and Tin Groups

Hydrogen sulphide precipitate: HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5, SnS, SnS_2. Treat with ammonium polysulphide.

Residue: HgS, PbS, Bi_2S_3, CuS, CdS.	Solution $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$, $(NH_4)_2SnS_3$. Add HCl.
	Precipitate: As_2S_5, Sb_2S_5, SnS_2. | Filtrate: NH_4Cl. Reject.

Analysis of the Copper Group

Residue from Ammonium Sulphide Treatment: HgS, PbS, Bi_2S_3, CuS, CdS. Boil with HNO_3.

Residue: HgS. Add Br_2 solution		Solution: Pb, Bi,Cu, Cd as nitrates. Add H_2SO_4, evaporate, add water.			
		Precipitate: $PbSO_4$. Dissolve in NH_4Ac. K_2CrO_4.	Filtrate: add NH_4OH.		
Residue: Sulphur.	Solution: $HgBr_2$. Add $SnCl_2$.		Precipitate: $Bi(OH)_3$. Add Na_2SnO_2.	Filtrate: $Cu(NH_3)_4SO_4$, $Cd(NH_3)_4SO_4$.	
	White or gray precipitate: Hg_2Cl_2 or Hg.	Yellow precipitate: $PbCrO_4$.	Black Residue: Bi.	To a small part add HAc and $K_4Fe(CN)_6$.	To the remainder add KCN and H_2S.
				Red precipitate: $Cu_2Fe(CN)_6$. White precipitate: $Cd_2Fe(CN)_6$.	Yellow precipitate: CdS. Solution $K_3Cu(CN)_4$.

Analysis of the Tin Group

Precipitate from Ammonium Sulphide Solution: As_2S_5, Sb_2S_5, SnS_2. Heat with 10 c.c. 12 normal HCl.

Solution: $SbCl_3$, $SnCl_4$. Dilute to 50 c.c., heat, and pass in H_2S.

Residue: As_2S_5. Dissolve in HCl and $KClO_3$.

Orange Precipitate: Sb_2S_3. Dissolve in HCl, add Sn and Pt.

Solution: $SnCl_4$. Cool, dilute, pass in H_2S.

Solution: H_3AsO_4. Add NH_4OH, NH_4Cl and $MgCl_2$.

Black deposit: Sb. Treat with NaClO.

Yellow Precipitate: SnS_2. Evaporate without filtering, add Pb, boil.

White, precipitate: $MgNH_4AsO_4$. Dissolve in HCl and add H_2S.

Black deposit: Sb.

Solution: $SnCl_2$. Add $HgCl_2$.

Yellow precipitate: As_2S_5, As_2S_3 and S.

White precipitate: Hg_2Cl_2.

Separation of the Aluminum and Iron Groups

The Ammonium Hydroxide and Ammonium Sulphide Precipitate: $Al(OH)_3$, $Cr(OH)_3$, FeS, ZnS, MnS, CoS,NiS. Dissolve in HCl and HNO_3, add NaOH.

Precipitate: $Fe(OH)_3$, $Mn(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$.
Solution: $NaAlO_2$, $NaCrO_2$, Na_2ZnO_2.
Add Na_2O_2 and filter.

Filtrate: $NaAlO_2$, Na_2CrO_4, Na_2ZnO_2.

Precipitate: $Fe(OH)_3$, $MnO(OH)_2$, $Co(OH)_3$, $Ni(OH)_2$.

Analysis of the Aluminum Group

Filtrate from the Sodium Hydroxide and Peroxide Treatment: Na_2ZnO_2, $NaAlO_2$, Na_2CrO_4. Acidify with HNO_3 and add NH_4OH.

Precipitate: $Al(OH)_3$. Dissolve in HNO_3, Add $Co(NO_3)_2$, evaporate, ignite.	Filtrate: add HAc and $BaCl_2$.	
Blue residue: $Co(AlO_2)_2$.	Precipitate: $BaCrO_4$. Dissolve in HCl and H_2SO_3, evaporate.	Filtrate: Zinc salt. Pass in H_2S.
	Green color: $CrCl_3$.	White precipitate: ZnS. Dissolve in HNO_3. Add $Co(NO_3)_2$ and Na_2CO_3, ignite.
		Green residue: $CoZnO_2$.

Analysis of the Iron Group

Precipitate produced by sodium hydroxide and peroxide:
A. Phosphate absent: $MnO(OH)_2$, $Fe(OH)_3$, $Co(OH)_3$, $Ni(OH)_2$, $Zn(OH)_2$.
B. Phosphate present: Also $BaCO_3$, $SrCO_3$, $CaCO_3$, $MgCO_3$, $FePO_4$, $Ca_3(PO_4)_2$, etc.
Dissolve in HNO_3 and H_2O_2, evaporate, heat with HNO_3 and $KClO_3$.

Precipitate: MnO_2. Add HNO_3 and bismuth peroxide.	Solution: Test a portion for a phosphate with $(NH_4)_2MoO_4$. A. Phosphate absent: add NH_4OH. B. Phosphate present: add NH_4Ac and $FeCl_3$, dilute and boil.		
Violet Color: $HMnO_4$.	Precipitate: A. $Fe(OH)_3$. B. Basic ferric acetate and $FePO_4$.	Filtrate: add NH_4OH, pass in H_2S.	
		Precipitate: ZnS, CoS, NiS.	Filtrate: A. Ammonium salts. Reject. B. Ba, Ca, Sr, Mg. Treat with Alkali-Earth group.

Separation of Zinc, Nickel and Cobalt

Hydrogen sulphide precipitate: ZnS, NiS, CoS. Treat with dil. HCl.

Solution: $ZnCl_2$, $NiCl_2$, $CoCl_2$, add NaOH and Na_2O_2.		Residue: NiS, CoS. Dissolve in HCl and HNO_3.
Filtrate: Na_2ZnO_2. Add HAc and H_2S.	Precipitate: $Ni(OH)_2$, $Co(OH)_3$, add HCl, evaporate.	
White precipitate: ZnS.	Residue: $NiCl_2$, $CoCl_2$, add HCl and ether.	
	Yellow residue: $NiCl_2$. Dissolve in water, add tartaric acid, NaOH and H_2S.	Blue solution: $CoCl_2$, evaporate, add HAc and KNO_2.
	Brown coloration: presence of nickel.	Yellow precipitate: $K_3Co(NO_2)_6$.

Analysis of the Alkaline-Earth Group

Ammonium carbonate precipitate: $BaCO_3$, $SrCO_3$, $CaCO_3$, $MgCO_3$, $(NH_4)_2CO_3$.
Dissolve in HAc, add NH_4Ac and K_2CrO_4.

Precipitate: $BaCrO_4$. Dissolve in HCl, evaporate.		Filtrate: add NH_4OH and alcohol.		
		Precipitate: $SrCrO_4$. Treat with $(NH_4)_2CO_3$.	Filtrate: Ca and Mg salts. Add $(NH_4)_2C_2O_4$.	
Test in flame.	Add HAc, NH_4Ac, and K_2CrO_4.			
Green Color: Ba.		Residue: $SrCO_3$. Dissolve in HAc. Add $CaSO_4$.	Precipitate: CaC_2O_4. Dissolve in dilute H_2SO_4, add alcohol.	Filtrate: add NH_4OH and Na_2HPO_4.
	Precipitate: $BaCrO_4$.			Precipitate: $MgNH_4PO_4$.
		Precipitate: $SrSO_4$.	Precipitate: $CaSO_4$.	

Analysis of the Alkali-Group

Filtrate from Ammonium Carbonate precipitate: NH_4, Na, K salts. Evaporate and ignite the residue.

Vapor: NH_4 salts.	Residue: KCl, NaCl. Add $HClO_4$, evaporate, add alcohol.	
	Residue: $KClO_4$. Dissolve in hot water, add $Na_3Co(NO_2)_6$.	Solution: $NaClO_4$. Saturate with HCl gas.
	Yellow precipitate: $K_2NaCo(NO_2)_6$.	Precipitate: NaCl. Dissolve in water, add $K_2H_2Sb_2O_7$.
		Crystalline precipitate: $Na_2H_2Sb_2O_7$.

Acidic Constituents

Detection of the Readily Volatile Acidic Constituents

Heat the substance with dilute H_2SO_4.

Vapors: CO_2, SO_2, H_2S, NO_2, Cl_2, Br_2, I_2, HCN. Expose to the vapors.

$Ba(OH)_2$ solution.	PbAc paper.	Starch and KI paper.	$Fe(OH)_2$ or $Fe(OH)_3$ and NaOH on paper.
White turbidity: $BaCO_3$ or $BaSO_3$. (Shows carbonate, sulphite or thiosulphate.)	Black color: PbS. (Shows sulphide.)	Blue color: I_2 (Shows nitrite, hypochlorite, chlorate, bromate, or iodide.)	Formation of $Na_4Fe(CN)_6$. Dip in HCl.
			Blue color: $Fe_4(Fe(CN)_6)_3$. (Shows cyanide.)

DETECTION OF THE ACIDIC CONSTITUENTS PRECIPITATED FROM ACID SOLUTIONS BY BARIUM AND SILVER SALTS

<table>
<tr><td colspan="4">To a HNO_3 solution of the substance add $BaCl_2$.</td><td colspan="3">To a HNO_3 solution of the substance add $Cd(NO_3)_2$.</td></tr>
<tr><td rowspan="3">Precipitate: $BaSO_4$. (Shows sulphate.)</td><td colspan="3">Filtrate: add Br_2.</td><td rowspan="2">Yellow precipitate: Cds. (Shows sulphide.)</td><td colspan="2">Filtrate: Add $AgNO_3$.</td></tr>
<tr><td rowspan="2">Precipitate: $BaSO_4$. (Shows sulphite.)</td><td colspan="2">Filtrate: add NH_4Ac.</td><td rowspan="2">Precipitate: AgCl, AgBr, AgI, $(Ag_2(CN)_2$, AgSCN, (Shows halides, cyanide or thiocyanates.)</td><td>Filtrate: $AgClO_3$, $AgBrO_3$. Add H_2SO_3.</td></tr>
<tr><td>Yellow precipitate $BaCrO_4$. (Shows chromate.)</td><td>Filtrate: add $CaCl_2$. Precipitate: CaF_2. (Shows fluoride.)</td><td>Precipitate: AgCl, AgBr. (Shows chlorate or bromate.)</td></tr>
</table>

DETECTION OF PHOSPHATE AND THE SEPARATE HALIDES

<table>
<tr><td colspan="4">To portions of the HNO_3 solution of the substance.</td></tr>
<tr><td>Add $(NH_4)_2MoO_4$.</td><td>Add $FeCl_3$.</td><td colspan="2">Add NaAc, HAc, $KMnO_4$ and $CHCl_3$.</td></tr>
<tr><td>Yellow precipitate: $(NH_4)_3PO_4$, $12MoO_3$. (Shows phosphate.)</td><td>Red color: $Fe(SCN)_3$. (Shows thiocyanate.)</td><td>Chloroform later, purple: I_2. (Shows iodide.)</td><td>Water layer: add H_2SO_4, more $KMnO_4$ and $CHCl_3$.</td></tr>
<tr><td colspan="2"></td><td>Chloroform layer, orange: Br_2. (Shows bromide.)</td><td>Water layer: Boil out the Br_2, add HNO_3 and $AgNO_3$.

Precipitate: AgCl. (Shows chloride.)</td></tr>
</table>

APPENDIX VII

BORAX BEAD TESTS

A borax bead is readily made by fusing borax in a small loop (about 3 mm.) of platinum wire. This is then touched to the unknown solid and the bead refused. The colors are for the cold bead unless otherwise indicated.

Element	Reducing Flame	Oxidizing Flame
Co	Blue	Blue
Cr	Green	Green
Cu	Red (if concentrated)	Blue
Fe	Green	Yellow
Mn	Colorless	Violet
Mo	Brown	Colorless
Ni	Grey	Violet (hot), Brown (cold)
Ti	Violet	Colorless
U	Green	Yellow
V	Green	Colorless
W	Yellow	Colorless

APPENDIX VIII

DENSITY OF WATER

Density of Water in Grams per Cubic Centimeter

t° C.	Density	t° C.	Density	t° C.	Density
0	0.999867	16	0.998969	32	0.995052
1	9926	17	8801	33	0.994728
2	9968	18	8621	34	4397
3	9992	19	8430	35	4058
4	1.000000	20	8229	36	0.993711
5	0.999992	21	8017	37	3356
6	9968	22	0.997795	38	0.992993
7	9929	23	7563	39	2622
8	9876	24	7321	40	0.992244
9	9808	25	7069	50	0.98804
10	9727	26	0.996808	60	0.98321
11	9632	27	6538	70	0.97778
12	9524	28	0.996258	80	0.97180
13	9404	29	0.995969	90	0.96531
14	0.999271	30	5672	100	0.95835
15	9126	31	5366	150	0.9173
				200	0.8628

Apparent Density of Water, When Weighed in Air with Brass Weights, in Grams per Cubic Centimeter

t °C.	Density	t° C.	Density	t °C.	Density
15	0.99805	20	0.99718	25	0.99604
16	.99790	21	.99697	26	.99579
17	.99774	22	.99676	27	.99552
18	.99756	23	.99653	28	.99524
19	.99738	24	.99629	29	.99496
				30	.99466

APPENDIX IX

DENSITY OF MERCURY

Density of Mercury in Grams per Cubic Centimeter

t °C.	Density	t °C.	Density	t °C.	Density
− 20	13.6450	15	13.5584	45	13.4849
− 10	6202	16	5560	50	4727
− 5	6078	17	5535	55	4605
0	5955	18	5511	60	4484
1	5930	19	5486	65	4362
2	5905	20	5461	70	4241
3	5880	21	5437	75	4120
4	5856	22	5412	80	3999
5	5831	23	5388	85	3878
6	5806	24	5363	90	3757
7	5782	25	5339	95	3637
8	5757	26	5314	100	3516
9	5732	27	5290	110	328
10	5708	28	5265	150	232
11	5683	29	5241	200	113
12	5658	30	5216	300	12.8760
13	5634	35	5094	400	6380
14	5609	40	4971	500	3950

APPENDIX X

EQUILIBRIUM PRESSURE OF WATER—WATER VAPOR

PRESSURE IN MM. OF MERCURY

(Cf. also Fig. 2, Chap. III)

t °C.	mm.	t °C.	mm.	t °C.	mm.
0	4.5687	39	51.997	78	327.05
1	4.9091	40	54.865	79	340.73
2	5.2719	41	57.870	80	354.87
3	5.6582	42	61.017	81	369.51
4	6.0693	43	64.310	82	384.64
5	6.5067	44	67.757	83	400.29
6	6.9718	45	71.362	84	416.47
7	6.4660	46	75.131	85	433.19
8	7.9909	47	79.071	86	450.47
9	8.5484	48	83.188	87	468.32
10	9.1398	49	87.488	88	486.76
11	9.7671	50	91.978	89	505.81
12	10.432	51	96.664	90	525.47
13	11.137	52	101.55	91	545.77
14	11.884	53	106.65	92	566.71
15	12.674	54	111.97	93	588.33
16	13.510	55	117.52	94	610.64
17	14.395	56	123.29	95	633.66
18	15.330	57	129.31	96	657.40
19	16.319	58	135.58	97	681.88
20	17.363	59	142.10	98	707.13
21	18.466	60	148.88	99	733.16
22	19.630	61	155.95	100	760.00
23	20.858	62	163.29	101	787.59
24	22.152	63	170.92	102	816.01
25	23.517	64	178.86	103	845.28
26	24.956	65	187.10	104	875.41
27	26.471	66	195.67	110	1075.37
28	28.065	67	204.56	120	1491.28
29	29.744	68	213.79	130	2030.28
30	31.510	69	223.37	140	2717.63
31	33.366	70	233.31	150	3581.2
32	35.318	71	243.62	160	4651.6
33	37.369	72	254.30	170	5961.7
34	39.523	73	265.38	180	7546.4
35	41.784	74	276.87	190	9442.7
36	44.158	75	288.76	200	11689.0
37	46.648	76	301.09	209	14042.5
38	49.259	77	313.85		

APPENDIX XI

TABLE OF SOLUBILITY PRODUCTS

The solubility product is the equilibrium constant for the solution of a solid strong electrolyte, e.g. for $Fe(OH)_2$, $K = (Fe^{++})\ (OH^-)^2$.

	K
Bromides	
AgBr	8×10^{-13}
CuBr	4×10^{-8}
TlBr	2×10^{-6}
Carbonates	
$PbCO_3$	3×10^{-14}
$BaCO_3$	8×10^{-9}
$SrCO_3$	2×10^{-9}
$CaCO_3$	9×10^{-9}
$MgCO_3$	3×10^{-5}
Ag_2CO_3	5×10^{-12}
Chlorides	
AgCl	1×10^{-10}
CuCl	1×10^{-6}
HgCl	3×10^{-18}
TlCl	2×10^{-4}
Chromates	
$PbCrO_4$	2×10^{-14}
$BaCrO_4$	2×10^{-10}
Ag_2CrO_4	3×10^{-12}
Fluorides	
CaF_2	3×10^{-11}
PbF_2	4×10^{-8}
MgF_2	7×10^{-9}
BaF_2	2×10^{-6}
Hydroxides	
$Ag_2O(Ag^+)(OH^-)$	1×10^{-8}
$Cr(OH)_3$	4×10^{-32}
$Cu(OH)_2$	2×10^{-13}
$Fe(OH)_2$	2×10^{-14}
$Fe(OH)_3$	1×10^{-38}
$Mg(OH)_2$	2×10^{-11}
$Mn(OH)_2$	4×10^{-14}
$Pb(OH)_2$	1×10^{-15}
$Zn(OH)_2$; $(Zn^{++})(OH^-)^2$	2×10^{-14}
$Zn(OH)_2$; $(H^+)(HZnO_2^-)$	7×10^{-30}
Iodates	
$Ba(IO_3)_2$	7×10^{-10}
$Ca(IO_3)_2$	6×10^{-7}
$Cu(IO_3)_2$	1×10^{-7}
$Pb(IO_3)_2$	2×10^{-13}
$Tl(IO_3)$	3×10^{-6}
Iodides	
PbI_2	2×10^{-8}
AgI	1×10^{-16}
CuI	5×10^{-12}
Oxalates	
CaC_2O_4	3×10^{-9}
MgC_2O_4	9×10^{-5}
$La_2(C_2O_4)_3$	2×10^{-28}
$Y_2(C_2O_4)_3$	5×10^{-25}
Sulfates	
$BaSO_4$	1×10^{-10}
$PbSO_4$	1×10^{-8}
$SrSO_4$	3×10^{-7}
Sulfides	
CdS	1×10^{-29}
Ag_2S	2×10^{-49}
CuS	8×10^{-45}
FeS	1×10^{-19}
HgS	1×10^{-53}
MnS	1×10^{-15}
NiS	1×10^{-24}
PbS	1×10^{-28}
ZnS	1×10^{-23}

APPENDIX XII

BUFFER SOLUTIONS

The following solutions may be employed to maintain desired concentrations of H^+ or OH^-. These concentrations are expressed as $pH = \log_{10} 1/(H^+)$ e.g., 0.01 *N* H^+ has a pH of 2.

Sorensen's Phosphate Solutions

KH_2PO_4, 9.078 g. per liter, and $Na_2HPO_4.2H_2O$, 11.876 g. per liter

Na_2HPO_4(cc.) .	0.25	0.5	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	9.5
KH_2PO_4 (cc.) . .	9.75	9.5	9.0	8.0	7.0	6.0	5.0	4.0	3.0	2.0	1.0	0.5
pH	5.29	5.59	5.91	6.24	6.47	6.64	6.81	6.98	7.17	7.38	7.73	8.04

Acetic Acid-Acetate Solutions, by Walpole-Clark

1 M CH_3COOH	0.185	0.176	0.164	0.147	0.126	0.102	0.080	0.059	0.042	0.019
1 M CH_3COONa	0.015	0.024	0.036	0.053	0.074	0.098	0.120	0.141	0.158	0.181
pH	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.6

Clark and Lubs, Borate Solutions

X cc. of 0.2 M NaOH added to 50 cc. of a mixture of 0.2 M H_3BO_3 + 0.2 M KCl and diluted to 200 cc.	cc.	2.61	3.97	5.90	8.50	12.00	16.30	21.30	26.70	32.00	36.85	40.80	43.90
	pH	7.8	8.0	8.2	8.4	8.6	8.8	9.0	9.2	9.4	9.6	9.8	10.0

APPENDIX XIII

INDICATORS

Clark and Lubs' List, Covering Range from Strong Acid to Strong Base

Abbreviations: c, colorless; r, red; y, yellow; b, blue; pu, purple; o, orange; v, violet.

Indicator	Useful range $pH = \log_{10} \frac{1}{(H^+)}$
Thymol blue	r 1.2–2.8 y
Bromphenol blue	y 3.0–4.6 b
Bromcresol green	y 3.8–5.4 b
Methyl red	r 4.2–6.3 y
Chlorphenol red	y 5.0–6.6 r
Bromcresol purple	y 5.2–6.8 pu
Bromthymol blue	y 6.0–7.6 b
Phenol red	y 6.8–8.4 r
Cresol red	y 7.2–8.8 r
Metacresol purple	y 7.6–9.2 pu
Thymol blue	y 8.0–9.6 b
O-cresolphthalein	c 8.2–9.8 r

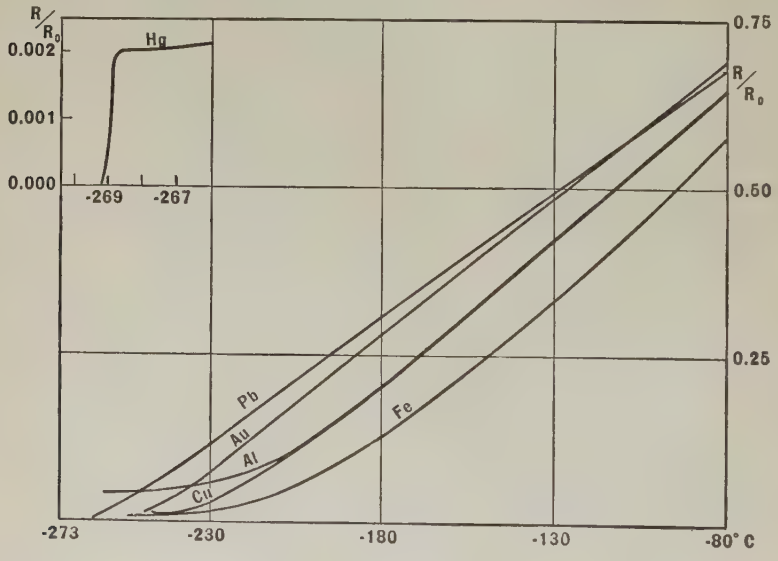
Indicators in Common Use

Indicator	pH range
Methyl orange	r 3.1 – 4.4 y
Resorcin blue	r 4.4 – 6.2 b
Litmus	r 4.5 – 8.3 b
Phenolphthalein	c 8.3 –10.0 r
Methyl violet	y 0.15 – 3.2 v
Trinitrobenzene	c 12.0 –14.0 o

APPENDIX XIV

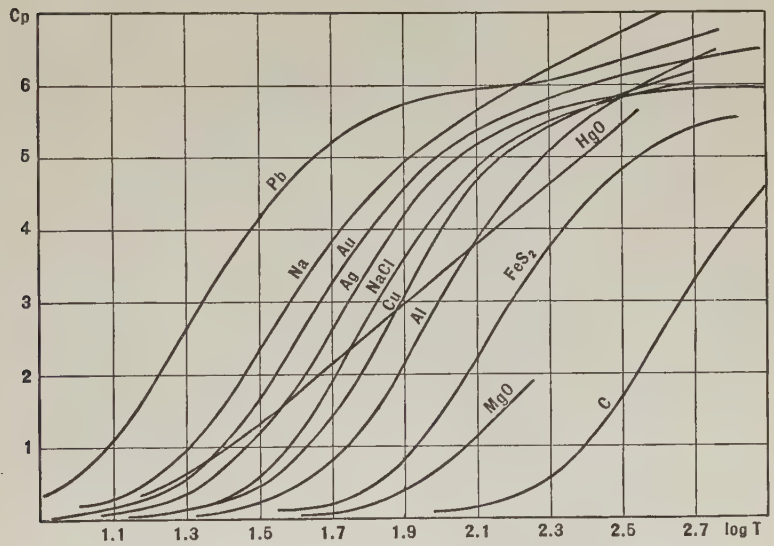
CHANGE OF RESISTANCE OF METALS WITH TEMPERATURE

R/R_0 is the ratio of the resistance to the value at 0° C. Insert shows supra-conductivity of mercury.



APPENDIX XV

SPECIFIC HEAT OF METALS AND COMPOUNDS AT LOW TEMPERATURES



APPENDIX XVI

TABLE OF COEFFICIENTS OF LINEAR EXPANSION

The coefficient of expansion is defined as $\alpha = (1/l)(dl/dt)$. The coefficient of cubical expansion is three times the coefficient of linear expansion.

Substance	t °C.	$\alpha \times 10^5$	Substance	t °C.	$\alpha \times 10^5$
Aluminum	− 188	0.881	Invar	15–100	0.15
	24	2.275	Iron	25–100	1.25
Antimony	17–100	1.08	Lead	17–100	2.93
Brass	40	1.85	Sodium chloride	− 188	2.78
Copper	− 153	1.203		27	3.99
	22	1.679	Silver	− 183	1.406
Diamond	50	0.13		25	1.896
Glass			Quartz—$\parallel$ to axis	− 188	0.24
Jena	30	0.75		27	0.764
Pyrex	− 174	0.11	Tin	40	2.22
	34	0.37	Zinc	10	2.97
Gold	17–100	1.45			

APPENDIX XVII

TABLE OF CONVERSION FACTORS

Values in agreement with International Critical Tables

Length and volume

1 Meter = 39.37 in. = (100/2.54) in.	
1 Yard (U.S.) = 91.44018 cm.	log = 1.9611371
1 Yard (British) = 91.43992 cm.	log = 1.9611350
1 Liter = 1000.027 $cm.^3$	log = 3.0000117
1 Cubic foot (U.S.) = 28317.0 $cm.^3$	log = 4.4520474
1 Gallon (U.S.) = 3785.4 $cm.^3$	log = 3.5781157
1 Gallon (British) = 4546.1 $cm.^3$	log = 3.6576376
1 Quart, dry (U.S.) = 1101-23 $cm.^3$	log = 3.0418770
1 Quart, liquid (U.S.) = 946.358 $cm.^3$	log = 2.9760557
1 Fluid ounce (U.S.) = 29.5737 $cm.^3$	log = 1.4709057

Weight

1 Grain = 64.799 mg.	log = 1.8115677
1 Ounce (avoirdupois) = 28.350 g.	log = 1.4525458
1 Pound (avoirdupois) = 453.59243 g. = 1000/2.2046223	log = 2.6566658
1 Ton, short (2000 pounds) = 907.185 kg.	log = 2.9576958
1 Ton, long (2240 pounds) = 1016.047 kg.	log = 3.0069138

Pressure

1 Pound weight per sq. in. (U.S.) = 68947.3 dynes $cm.^{-2}$	log = 4.8385173
1 Centimeter of water at 4° C. = 980.638 dynes $cm.^{-2}$	log = 2.9915090
1 Inch of water at 4° C. (U.S.) = 2490.827 dynes $cm.^{-2}$	log = 3.3963436
1 Centimeter of mercury at 0° C. = 13332.24 dynes $cm.^{-2}$	log = 4.1249031
1 Inch of mercury at 0° C. (U.S.) = 33863.95 dynes $cm.^{-2}$	log = 4.5297377

Density

1 Gram per milliliter = specific gravity, t°/4° = 0.999973 g. $cm.^{-3}$	log = $\bar{1}$.9999883
1 Pound per cu. in. (U.S.) = 27.67974 g. $cm.^{-3}$	log = 1.4221621
1 Pound per cu. ft. (U.S.) = 0.016018 g. $cm.^{-3}$	log = $\bar{2}$.2046183
1 Pound per gal. (U.S.) = 0.1198257 g. $cm.^{-3}$	log = $\bar{1}$.0785502

Energy

1 Cubic centimeter-atmosphere 0.10133 = 0.101325 joules (absolute)	log = $\bar{1}$.0057167
1 Gram calorie (15°) = 4.185 joules absolute	log = 0.6216955
1 British Thermal Unit (39° F.) = 1060.4 joules (abs.)	log = 3.0254697
1 British Thermal Unit (mean) = 1054.8 joules (abs.)	log = 3.0231701
1 British Thermal Unit (60° F.) = 1054.6 joules (abs.)	log = 3.0230878

Work

1 Watt (International) = 1.00032 watt (absolute)	log = 0.0001390
1 Kilogram-meter per sec. = 9.80665 watt (absolute)	log = 0.9915207
1 Foot-pound per sec. (U.S.) = 1.355821 watt (abs.)	log = 0.1322022
1 Horsepower (U.S., British) = 746.00 watt (abs.)	log = 2.8727388
1 Horsepower (Continental Europe) = 736.00 watt (abs.)	log = 2.8660778
1 Cheval-vapeur (75 kg.-m. per sec.) = 735.499 watt (abs.)	log = 2.8665820

Temperature

Fahrenheit $x°$ F. = (5/9) $(x - 32)°$ C.
Reaumur x° R. = (5/4) x° C.

APPENDIX XVIII

THE ELECTRON STRUCTURE OF THE ELEMENTS

Atomic Number	Element	Number of Electrons in Each Quantum Group																		
		1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1	6_2	6_3	7_1	7_2
1	H	1																			
2	He	2																			
3	Li	2	1																		
4	Be	2	2																		
5	B	2	2	1																	
6	C	2	2	2																	
7	N	2	2	3																	
8	O	2	2	4																	
9	F	2	2	5																	
10	Ne	2	2	6																	
11	Na	2	2	6	1																
12	Mg	2	2	6	2																
13	Al	2	2	6	2	1															
14	Si	2	2	6	2	2															
15	P	2	2	6	2	3															
16	S	2	2	6	2	4															
17	Cl	2	2	6	2	5															
18	A	2	2	6	2	6															
19	K	2	2	6	2	6		1													
20	Ca	2	2	6	2	6		2													
21	Sc	2	2	6	2	6	1	2													
22	Ti	2	2	6	2	6	2	2													
23	V	2	2	6	2	6	3	2													
24	Cr	2	2	6	2	6	4	2													
25	Mn	2	2	6	2	6	5	2													
26	Fe	2	2	6	2	6	6	2													
27	Co	2	2	6	2	6	7	2													
28	Ni	2	2	6	2	6	8	2													
29	Cu	2	2	6	2	6	10	1													
30	Zn	2	2	6	2	6	10	2													
31	Ga	2	2	6	2	6	10	2	1												
32	Ge	2	2	6	2	6	10	2	2												
33	As	2	2	6	2	6	10	2	3												
34	Se	2	2	6	2	6	10	2	4												
35	Br	2	2	6	2	6	10	2	5												
36	Kr	2	2	6	2	6	10	2	6												
37	Rb	2	2	6	2	6	10	2	6			1									
38	Sr	2	2	6	2	6	10	2	6			2									
39	Y	2	2	6	2	6	10	2	6	1		2									
40	Zr	2	2	6	2	6	10	2	6	2		2									
41	Cb	2	2	6	2	6	10	2	6	3		2									
42	Mo	2	2	6	2	6	10	2	6	4		2									
43	Ma	2	2	6	2	6	10	2	6	5		2									
44	Ru	2	2	6	2	6	10	2	6	6		2									
45	Rh	2	2	6	2	6	10	2	6	7		2									

THE ELECTRON STRUCTURE OF THE ELEMENTS (Cont'd)

Atomic Number	Element	Number of Electrons in Each Quantum Group																		
		1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1	6_2	6_3	7_1	7_2
46	Pd	2	2	6	2	6	10	2	6	8		2									
47	Ag	2	2	6	2	6	10	2	6	10		1									
48	Cd	2	2	6	2	6	10	2	6	10		2									
49	In	2	2	6	2	6	10	2	6	10		2	1								
50	Sn	2	2	6	2	6	10	2	6	10		2	2								
51	Sb	2	2	6	2	6	10	2	6	10		2	3								
52	Te	2	2	6	2	6	10	2	6	10		2	4								
53	I	2	2	6	2	6	10	2	6	10		2	5								
54	Xe	2	2	6	2	6	10	2	6	10		2	6								
55	Cs	2	2	6	2	6	10	2	6	10		2	6				1				
56	Ba	2	2	6	2	6	10	2	6	10		2	6				2				
57	La	2	2	6	2	6	10	2	6	10		2	6	1			2				
58	Ce	2	2	6	2	6	10	2	6	10	1	2	6	1			2				
59	Pr	2	2	6	2	6	10	2	6	10	2	2	6	1			2				
60	Nd	2	2	6	2	6	10	2	6	10	3	2	6	1			2				
61	Il	2	2	6	2	6	10	2	6	10	4	2	6	1			2				
62	Sa	2	2	6	2	6	10	2	6	10	5	2	6	1			2				
63	Eu	2	2	6	2	6	10	2	6	10	6	2	6	1			2				
64	Gd	2	2	6	2	6	10	2	6	10	7	2	6	1			2				
65	Tb	2	2	6	2	6	10	2	6	10	8	2	6	1			2				
66	Dy	2	2	6	2	6	10	2	6	10	9	2	6	1			2				
67	Ho	2	2	6	2	6	10	2	6	10	10	2	6	1			2				
68	Er	2	2	6	2	6	10	2	6	10	11	2	6	1			2				
69	Tu	2	2	6	2	6	10	2	6	10	12	2	6	1			2				
70	Yb	2	2	6	2	6	10	2	6	10	13	2	6	1			2				
71	Lu	2	2	6	2	6	10	2	6	10	14	2	6	1			2				
72	Hf	2	2	6	2	6	10	2	6	10	14	2	6	2			2				
73	Ta	2	2	6	2	6	10	2	6	10	14	2	6	3			2				
74	W	2	2	6	2	6	10	2	6	10	14	2	6	4			2				
75	Re	2	2	6	2	6	10	2	6	10	14	2	6	5			*2				
76	Os	2	2	6	2	6	10	2	6	10	14	2	6	6			*2				
77	Ir	2	2	6	2	6	10	2	6	10	14	2	6	7			*2				
78	Pt	2	2	6	2	6	10	2	6	10	14	2	6	8			*2				
79	Au	2	2	6	2	6	10	2	6	10	14	2	6	10			1				
80	Hg	2	2	6	2	6	10	2	6	10	14	2	6	10			2				
81	Tl	2	2	6	2	6	10	2	6	10	14	2	6	10			2	1			
82	Pb	2	2	6	2	6	10	2	6	10	14	2	6	10			2	2			
83	Bi	2	2	6	2	6	10	2	6	10	14	2	6	10			2	3			
84	Po	2	2	6	2	6	10	2	6	10	14	2	6	10			2	4			
85	——	2	2	6	2	6	10	2	6	10	14	2	6	10			2	5			
86	Rn	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6			
87	——	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6		1	
88	Ra	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6		2	
89	Ac	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6	1	2	
90	Th	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6	2	2	
91	Pa	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6	3	2	
92	U	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6	4	2	

*One of these electrons may be in the 5_3 level.

APPENDIX XIX

TABLE OF DENSITIES, MELTING POINTS, BOILING POINTS, COLORS, AND SOLUBILITIES OF INORGANIC COMPOUNDS

Values for densities are in grams per cc. Temperatures 15–25° C. Values for solubilities are in grams of anhydrous salt per 100 grams of water solution.

Abbreviations for colors: bk, black; bl, blue; br, brown; c, colorless or white if finely divided; d, dark; gr, green;gy, grey; l, light; or, orange; pk, pink; pu, purple; r, red; ro, rose; sil, silver; v, violet; w, white; y, yellow.

Formula	Density	Melting Point °C.	Boiling Point °C.	Color	Solubility in Water
Aluminum					
Al	2.71	658	1800	gy-w	sol. H^+ and OH^-
Al_2O_3	4.00	2050		c	v. sl. sol.
$Al_2O_3 \cdot H_2O$	3.41	d. 360		c	0.0001(20°)
$Al(C_2H_3O_2)_3$		d.		c	sol. but hydr.
$Al(C_2H_3O_2)_2OH$				c	sl. sol.
$Al(BrO_3)_3 \cdot 9H_2O$		62.3		c	sol.
$AlBr_3$	3.01	97.5	265	c	sol.
Al_4C_3	2.36	high		y	giv. $Al(OH)_3 + CH_4$
$Al(ClO_3)_3 \cdot 6H_2O$		d.		c	v. sol.
$AlCl_3$	2.44	190 (2½ at.)	194	c	6 aq. 41.1(15°)
$AlCl_3 \cdot 3NH_3$		d. 280		c	giv. $Al(OH)_3$
AlF_3	3.07	1040		c	sl. sol.
$Al(OH)_3$	2.3	d.		c	v. sl. sol.
AlI_3	3.98	191	360	c	6 aq. v. sol.
$Al(NO_3)_3 \cdot 9H_2O$		73	d. 134	c	4 aq. 38.9(25°)
AlN		2150		gy	not sol.
$AlPO_4$	2.59	high		c	v. sl. sol.
$Al_2(SO_4)_3$	2.7	d. 770		c	18 aq. 26.6(20°),
$AlNH_4(SO_4)_2 \cdot 12H_2O$	1.64	93		c	6.2(20°), 26.0(80°)
Al_2S_3	2.02	1100		y	hydr.
$AlTl(SO_4)_2 \cdot 12H_2O$	2.32	91		c	5.1(15°)
$AlK(SO_4)_2 \cdot 12H_2O$	1.76	84.5		c	4.8(15°), 60.6(100°)
$Al_6O_4 \cdot Si_2O_4$	3.15	d. 1810		c	v. sl. sol.
Ammonia					
NH_3	0.82(79°)	− 77.7	− 38.5	c	89.9(0°), 7.4(100°)
NH_4OH		− 79	d.	c	cf. NH_3
$(NH_4)_2O$		− 79	d.	c	
$NH_4C_2H_3O_2$ (acetate)		89.0		c	148(4°)
$NH_4H_2AsO_4$	2.31			c	sol.
NH_4AsO_2				c	v. sol
NH_4Br	2.55			c	41.1(15°), 56.1(100°)
$(NH_4)_2CO_3 \cdot H_2O$		d. 85°		c	100(15°)
NH_4HCO_3	1.59			c	11.9(0°), 30.0(60°)
NH_4Cl	1.54			c	22.9(0°), 29.3(30°)
NH_4ClO_4	1.95	d.		c	20.8(20°), 57(100°)
$(NH_4)_2CrO_4$	1.8	d. 180°		y	40(30°)
NH_4CNO		d.		c	sol.
NH_4CN		d. 36°		c	sol.
$(NH_4)_2Cr_2O_7$	2.15	d.		r–br	47.1(30°)
NH_4F				c	v. sol.
NH_4I	2.56			c	176 g./110 g. H_2O at 25°
NH_4IO_3	3.31	d. 150		c	4.2(0°), 0.6(24°)
$NH_4MgAsO_4 \cdot 6H_2O$	1.93			c	0.038(20°)
$NH_4MgPO_4 \cdot 6H_2O$	1.65			c	0.024(15°)
$(NH_4)_2Mo_4O_{13} \cdot H_2O$	2.27			c	3.7(18°)
NH_4NO_3	α1.66	169.6	d. 210	c	
	β1.72				70(30°)

Table of Densities, Melting Points, etc. (Cont'd)

Formula	Density	Melting Point °C	Boiling Point °C	Color	Solubility in Water
NH_4NO_2				c	sol.
$(NH_4)_2C_2O_4 \cdot H_2O$	1.50			c	4.2(20°), 9.3(50°)
NH_4MnO_4	2.21	d.		g	8(15°)
$(NH_4)_2S_2O_8$	1.98	d. 120		c	58.2(0°)
$(NH_4)_2PtCl_6$	3.06	d.		y	0.67(20°), 1.25(100°)
$(NH_4)_2PtCl_4$		d.		y	sol.
$(NH_4)_2PdCl_6$	2.42	d.		r	sl. sol.
$(NH_4)_2HPO_4$	1.619			c	25
$NH_4H_2PO_4$	1.803			c	18.0(50°)
$(NH_4)_3PO_412MoO_3 \cdot 3H_2O$				y	0.03(15°)
$(NH_4)_2SO_4$	1.77	140		c	41.4(0°), 43.8(30°)
$(NH_4)_2S$		d.		y	v. sol. giv. HS^-
$(NH_4)_2SO_3 \cdot H_2O$		d.		c	v. sol.
$(NH_4)_2Se$			d.	br	sol.
NH_4CNS	1.31(13°)	− 159	d. 170	c	55(0°), 62(20°)
$(NH_4)_2C_4H_4O_6$	1.60			c	5.9(15°)
Antimony					
Sb	6.68	630.5	1380	gr	not sol.
H_3SbO_4	6.6	d.		c	sl. sol.
H_3SbO_3		d.		c	v. sl. sol.
Sb_2O_3	5.67	656	15.5	c	0.002(15°)
SbO_2	4.07	1060		c	v. sl. sol.
Sb_2O_5	3.78	450	1060	y	v. sl. sol.
$SbBr_3$	4.15	96.6	280	y	sol. hydr.
$SbCl_3$	3.14	73.4	223.5	c	910 g./100 g. H_2O at 20°
$SbCl_5$	2.34	2.8	92 at 30 mm.	c	hydr.
SbF_3	4.38	292		c	83(25°)
SbF_5	2.99	7		c	hydr.
SbH_3	2.26 l.q.	− 88	− 18	c	0.12 (1 atm.p.)
SbI_3 Trig	4.85	167	401	y	hydr.
M	4.77			r	
SbI_5		79			
SbOCl		d. 170		c	v. sl. sol.
$Sb_4O_5Cl_2$	5.01			c	v. sl. sol.
$Sb_2(SO_4)_3$	3.63	d.		c	hydr.
Sb_2S_3	4.64	550		bk, r	0.000175
Sb_2S_5	4.12			or	v. sl. sol.
Sb_2Se_3		611		gy	v. sl. sol.
Sb_2Te_3		629		gy	
$(SbO)KC_4H_4O_6 \cdot \frac{1}{2}H_2O$	2.61	½ aq. 100		c	7.0(25°)
Arsenic					
As	5.7	814 (36 atm.)	615	sil	not sol.
$H_3AsO_4 \cdot \frac{1}{2}H_2O$	2–2.5	35.5	1 aq, 160	c	186.3(20°)
$H_4As_2O_7$		206 d.		c	sol.
As_2O_3	3.65–4.15	218 sub.		c	2.04(25°)
As_2O_5	4.15	315		c	cf. H_3AsO_4
$AsBr_3$	3.54	328		y	sol.
$AsCl_3$	2.16	− 18	130.2	c	sol.
$AsCl_5$		− 40		c	hydr.
AsF_3	2.66			c	hydr.
AsF_5		− 80		c	hydr.
AsH_3		− 113.5		c	sl.sol.
AsI_3	4.39	146		or–r	6(25°)
AsI_5	3.93			br	hydr.
AsOCl				br	sol.

Table of Densities, Melting Points, etc. (Cont'd)

Formula	Density	Melting Point °C	Boiling Point °C	Color	Solubility in Water
As_2S_2 α, β	α3.51				
	β3.25	β307	565	r	v.sl.sol.
As_2S_3	3.43	300	700	r & y	0.00005
As_2S_5		sub.		y	v.sl.sol.
Barium					
Ba	3.5	850	1140	y–w	giv. $Ba(OH)_2 + H_2$
BaO	5.72	1923		c	9 aq. 3.36(20°), 47.6(80°
BaO_2	4.96	450		gy	v.sl.sol.
$Ba(C_2H_3O_2)_2 \cdot H_2O$	2.19	d.		c	43.3(26°)
$BaHAsO_4 \cdot H_2O$	3.93	d.		c	sl.sol.
$Ba(BrO_3)_2 \cdot H_2O$	3.99			c	0.3(0°), 5.67(100°)
$BaBr_2 \cdot 2H_2O$	3.58	an. 847		c	151(20°), 60(100°)
$BaCO_3$ α, β	α4.43	β1740(90 atm.)	d.	c	0.002(20°), 0.006(100°)
$Ba(ClO_3)_2 \cdot H_2O$	3.18	d. 120		c	21.5(25°), 33.9(100°)
$BaCl_2 \cdot 2H_2O$	3.10	an. 962		c	26.3(20°), 37.0(100°)
$BaCrO_4$	4.50			y	0.00038(20°)
BaF_2	4.83	1280		c	0.16(18°)
BaH_2	4.21	d. 675		c	giv.$Ba(OH)_2 + H_2$
$Ba(OH)_2 \cdot 8H_2O$	2.13	77.9	103	c	cf. BaO
$Ba(IO_3)_2 \cdot H_2O$	5.01	aq. 130		c	0.028(20°), 0.20(100°)
BaI_2	5.15	d. 740		c	6 aq. 66.5(20°)
$Ba(NO_3)_2$	3.24	592	d.	c	1 aq. 38.6(20°)
BaC_2O_4	2.66	d.		c	2 aq. 0.0009(25°)
$Ba(ClO_4)_2$		505		c	66.5(25°)
$Ba(MnO_4)_2$				gr	62.5(11°), 75.4(25°)
$BaMoO_4$				c	0.0058(23°)
$Ba_3(PO_4)_2$	4.11			c	v.sl.sol.
$BaH_4(PO_4)_2$	2.90			c	sol.
$BaHPO_4$	4.16			c	0.01(20°)
$Ba_2P_2O_7$	4.11			c	0.01
$BaSO_4$	4.50	1580		c	0.00024(20°)
$BaSO_3$			d.	c	0.02(20°)
BaS	4.25	high		gy–gr	hydr.
Beryllium					
Be	1.85	1350	1500	c	0.36(0°)
BeO	3.03	2400		c	2×10^{-5}(20°)
$Be(OH)_2$		d.		w	0.025 in *N* NaOH(20°)
$BeBr_2$		490		c	sol.
$BeCO_3 \cdot 4H_2O$				c	0.36(0°)
$BeCl_2$	1.90	440	500	c	v. sol.
BeF_2	2.1	ca. 800		c	giv.oxy-salt
BeI_2	4.20	510	590	c	sol.
$Be(NO_3)_2 \cdot 3H_2O$		60		c	sol.
$BeC_2O_4 \cdot 3H_2O$				c	40 g./100 g. H_2O at 25°
$BeSO_4 \cdot 4H_2O$	1.71	2 aq. 100	d.	c	29.8(25°)
Bismuth					
Bi	9.80	271	1450	gy–w	not sol.
$HBiO_3$	5.75	d. 120		r	evol. O_3
Bi_2O_3	8.9	820		y	v.sl.sol.
Bi_2O_5	5.10	150	357	r	v.sl.sol.
$Bi(OH)_3$		100		c	0.00014
$BiBr_3$	5.7	218	453	y	hydr.
$Bi_2O_2CO_3 \cdot H_2O$	6.86	d.		c	v.sl.sol.
$BiCl_2$				v	d.
$BiCl_3$	4.7	230	447	c	hydr. sol. in HCl
$BiCl_4$		225		c	d.
BiOCl	7.72	high		c	v.sl.sol.
BiOF	7.5			c	v.sl.sol.
BiI_3	5.7	439		gy–bl	hydr.

Table of Densities, Melting Points, etc. (Cont'd)

Formula	Density	Melting Point °C	Boiling Point °C	Color	Solubility in Water
$Bi(NO_3)_3 \cdot 5H_2O$	2.83	d. 30		c	v.sol. in dil. HNO_3
$BiONO_3 \cdot H_2O$	4.93	d. 260		c	v.sl.sol.
$BiPO_4$	3.23			c	v.sl.sol.
BiS	7.7	685		gy	v.sl.sol.
Bi_2S_3	7.39	d.		br	0.000018(18°)
$Bi_2(SO_4)_3$				c	hydr. sol. in H_2SO_4
Boron					
B	2	2300	2250	br	not sol.
H_3BO_3	1.43	185		c	4.8(20°), 28.7(100°)
B_2O_3	1.85			c	cf. H_3BO_3
BBr_3	l. 2.60	− 45			hydr.
B_6C	2.6	2350		bk	not sol.
BCl_3	l. 1.43	− 107	18.23	c	hydr.
BF_3		− 127		c	1.06 cc/cc H_2O at 0°, 1 atm.
B_2H_6		− 169		c	sl.sol.
B_4H_{10}		− 112		c	sl.sol.
$B_{10}H_{14}$	0.94	99.5		c	sl.sol.
BI_3	l. 3.35	43		c	hydr.
BN				c	not sol.
B_2S_3	1.55	310		c	hydr.
Bromine					
Br_2	3.4	− 7.2	58.78	br	4.0(0°), 3.3(25°)
$HBrO_3$		d. 100		l–y	v.sol.
$BrCl \cdot 10H_2O$		7	d. 10	y	v.sol.hydr.
BrF_3		5		y	hydr.
Cadmium					
Cd	8.6	320.9	778	sil	v.sl.sol.
CdO	8.15			br	cf. $Cd(OH)_2$·Sol. H^+
$Cd(OH)_2$	4.79	d. 300		c	0.00026(25°)
$Cd(C_2H_3O_2)_2 \cdot 3H_2O$	2.01			c	v.sol.
$CdBr_2$	5.19	583	810	y	4 aq. 48.8(18°)
$CdCO_3$	4.26	d. < 500		c	v.sl.sol.
$CdCl_2 \cdot 2.5H_2O$	3.32	an. 568		c	56.3(30°)
CdF_2	6.64	1100		c	4.3(25°)
CdI_2 α, β	α5.67	α388	α715	br	α 46.0(18°)
	β5.30				
$Cd(NO_3)_2 \cdot 4H_2O$	2.45	59.4	132	c	58.4(30°)
CdC_2O_4	3.32	34		c	0.0033(18°)
$Cd_3(PO_4)_2$		1500		c	v.sl.sol.
$CdSiO_3$	4.93	1242		c	v.sl.sol.
$3CdSO_4 \cdot 8H_2O$	3.09			c	43.4(26°), 1 aq. 60.8-(100°)
$CdSO_4$	4.69	100		c	
CdS	4.8	1750(100) atm.		y	0.00013(18°)
Calcium					
Ca	1.55	810	1170	sil	$Ca(OH)_2 + H_2$
CaO	3.40	25.72		c	cf.$Ca(OH)_2$
$Ca(OH)_2$	2.34	d.		c	0.165(20°), 0.08(100°)
$Ca(C_2H_3O_2)_2 \cdot H_2O$		d.		gy	25.8(20°), 22.9(100°)
$CaBr_2 \cdot 6H_2O$		38.2	150	c	60.5(25°)
$CaBr_2$	3.35	765	806–812	c	6 aq. 58.8(20°)
CaC_2	2.22	2300		gy	giv.$Ca(OH)_2 + C_2H_2$
$CaCO_3$ (Aragonite)	2.93		d.	c	0.00153(25°)
$CaCO_3$ (Calcite)	2.71	1339	d.	c	0.00143(25°)
$CaCl_2$	2.15	772		c	cf. 6 aq.
$CaCl_2 \cdot 6H_2O$	1.68	29.92	129.130	c	42.7(20°), 2 aq. 61.4 (100°)
$CaCrO_4$			d.	y	2 aq. 14(20°), an. 2.3-(18°)

Table of Densities, Melting Points, etc. (Cont'd)

Formula	Density	Melting Point °C	Boiling Point °C	Color	Solubility in Water
CaF_2	3.18	1360		c	0.0037(15°)
CaH_2	1.7	d. 675		c	giv. $Ca(OH)_2 + H_2$
$Ca(ClO)_2 \cdot 4H_2O$		d.		c	v. sol.
CaI_2	3.96	575	708–719	y–w	6 aq. 67(20°)
Ca_3N_2	2.63	900		l–br	hydr. slowly
$Ca(NO_3)_2 \cdot 4H_2O$ α, β	α1.82	α42.7	132	c	54.8(18°)
CaC_2O_4	2.2			c	0.0006(18°), 0.0014(95°)
$Ca(MnO_4)_2 \cdot 4H_2O$		d.		pu	v. sol.
Ca_3P_2	2.51	> 1600		gy	giv. PH_3
$Ca_3(PO_4)_2$	3.14	1670		c	0.0023–.0031
$CaHPO_4 \cdot 2H_2O$	2.31	d.		c	0.02(24.5°)
$CaH_4(PO_4)_2 \cdot H_2O$	2.22	d.		c	1.8(30°)
$Ca_2P_2O_7$	3.09	1230		c	sl. sol.
$Ca(H_2PO_2)_2$		d.		c	sol.
$3Ca_3(PO_4)_2 \cdot CaFCl$	3.14	1270		c	v.sl.sol.
$CaSO_4$	2.96	1450		c	cf. 2 aq.
$CaSO_4 \cdot 2H_2O$	2.32	2 aq. below 300°		c	0.208(25°)
CaS	2.81			c	hydr.
$CaSO_3$				c	0.17(15°)
$CaSeO_4$	2.93			c	2 aq. 7.6(20°)
Carbon					
C (diamond)	3.51		4200	c	
C (graphite)	2.25	3500	4200	bl	v.sl.sol.
CO	l. 0.81	− 207	− 190	c	0.0044(0°), 0.0018(50°)
CO_2	s. 1.53 l. 1.10	s. − 566		c	0.335(0°), 0.145(20°), 0.06(60°)
C_3O_2	1.11	− 107	135	c	giv. malonic acid
CBr_4	3.42	α48.4 / β90.1	189.5	w	v.sl.sol.
CCl_4	1.59	− 23.0	76.8	c	0.08(20°)
CF_4		− 80	− 15	c	sl. sol.
CI_4	4.32	d.		r	hydr.
COS	1.24	− 138	− 48	c	0.122(25°)
CS_2	1.26	− 111.6	46.3	c	0.18(20°)
C_2N_2	0.87	− 34.4	− 20.5	c	sl.sol.: $(C_2N_2)_n$ more sol.
Cerium					
Ce	6.9	640	1400	gy	v.sl.sol.
Ce_2O_3	6.9			gy	v.sl.sol.
CeO_2	7.3	1950		l–y	v.sl.sol.
$CeCl_3$	3.92	848		r–w	sol.
$Ce_2(CO_3)_3 \cdot 5H_2O$				c	v.sl.sol.
CeF_3	5.8	1324		c	v.sl.sol.
$Ce(IO_3)_4$				c	0.015(20°)
$Ce(NO_3)_3 \cdot 6H_2O$		3 aq. 150	d. 200	r	sol.
$Ce(NO_3)_4$				y	sol.
$Ce_2(C_2O_4)_3 \cdot 9H_2O$				c	4×10^{-5}(25°)
$Ce_2(SO_4)_3$	3.91			c	8 aq. 8.7(20°)
$Ce(SO_4)_2 \cdot 4H_2O$				y	sol.
Cesium					
Cs	1.90	26	670	sil.	$Cs(OH_2) + H_2$
Cs_2O	4.36			or	giv.CsOH
Cs_2O_3	4.25	400		gy	d.
Cs_2O_4		600		y	giv. $CoOH + HO_2^-$
CsOH	3.67	272.5		c	79.4(15°)
CsBr	4.44	636		c	sol.
Cs_2CO_3			d. 610	c	v. sol.
CsCl	3.97	646		c	65(20°), 73(100°)
CsF	3.59	683		c	1.5 aq. v. sol.
CsI	4.51	621		c	28(0°), 51.5(35.6°)

Table of Densities, Melting Points, etc. (Cont'd)

Formula	Density	Melting Point °C	Boiling Point °C	Color	Solubility in Water
$CsNO_3$	3.68	414	d.	c	18.7(20°), 66.3(100°)
Cs_2SO_4	4.24	1010		c	164(20°), 69(100°)
Chlorine					
Cl_2	s. 1.9	− 101.6	− 34.6	l–y	0.63(25°)
$Cl_2 \cdot 8H_2O$	1.23	d. 9.6		l–y	1.85(20°) Under P.
$HClO_3 \cdot 7H_2O$	1.28	d.		c	v.sol.
$HClO_4$	l. 1.77	− 112		c	1 aq. 77.7(17°)
Cl_2O	0.00385	− 20	5	y–r	2 vol/vol H_2O at O°
ClO_2	0.00298	− 76	9.9	r	10.8(18°)
Chromium					
Cr	7.1	1615	2200	sil	not sol.
CrO_3	2.7	d. 190	d.	r	62.8(25°)
Cr_2O_3	5.21	1900		gr	v.sl.sol.
$Cr(OH)_2$				y. br	evol.$_2$ H
$Cr(OH)_3 \cdot 2H_2O$				gr	v.sl.sol.
$CrCl_2$	2.75			bl	v.sol.
$CrCl_3$	2.7		1200–1500	v	70(25°) v. slowly sol.
Cr_3C_2	6.68	1890			not sol.
CrF_3	3.8	> 1000		gr	v. sol.
$Cr(NO_3)_3 \cdot 9H_2O$		36.5	125.5	pu	sol.
$Cr(PO_4) \cdot 3H_2O$				bl.gr.	sl.sol.
$CrSO_4 \cdot 7H_2O$				bl	12 g. 7 aq/100 g.H_2O(0°)
$Cr_2(SO_4)_3 \cdot 18H_2O$	1.7	12 aq. 100		v	120 g. 18 aq/100 g.H_2O-(20°)
Cr_2S_3	3.7			d-br	hydr. slowly
Cobalt					
Co	8.9	1480	2900	gy–w	not sol.
CoO	5.68	d. 800		br	v.sl.sol.
Co_2O_3	5.18			br	v.sl.sol.
Co_3O_4	6.07			bl	v.sl.sol.
$Co(OH)_2$	3.60	d.		r	v.sl.sol.
$Co(OH)_3$				bl	3.2×10^{-4}
$Co(C_2H_3O_2)_2 \cdot 4H_2O$	1.72			v	sol.
$Co_3(AsO_4)_2 \cdot 8H_2O$	2.9			r	v.sl.sol.
$CoBr_2 \cdot 6H_2O$		d. 100		r	67(60°)
$CoCO_3$	4.13	d.		ro	v.sl.sol.
$Co(CO)_4$	1.73	51	d. 135	or	v.sl.sol.
$CoCl_2 \cdot 6H_2O$	1.92	86		r	33.3(20°)
$CoCl_3$	2.94	d.		r	sol.
CoI_2	5.68			v	2 aq. 79(46°)
$Co(NO_3)_2 \cdot 6H_2O$	1.88	< 100		r	49.7(18°)
$Co_3(PO_4)_2 \cdot 3H_2O$				l–r	v.sl.sol.
$CoSO_4 \cdot 7H_2O$	1.95			r	26.6(20°), 45.3(100°)
$Co_2(SO_4)_3$				bl	hydr.
CoS	5.45	< 1100		br	0.00038
Columnium					
Cb	8.4	1950	3300		not sol.
Cb_2O_5	4.61	1520		c	v.sl.sol.
CbF_5	3.29	75.5	219	c	hydr.
$CbCl_5$	2.75	194	240.5	y	hydr.
$CbOCl_3$			s. 400	c	sol., hydr.
Copper					
Cu	8.92	1083	2300	r	v.sl.sol.
Cu_2O	6.0	1235	1800	r	v.sl.sol.
CuO	6.4	d. 1026 at 153 mm. O_2		bk	v.sl.sol.
$Cu(OH)_2$	3.68	d.		bl	v.sl.sol.
$Cu(C_2H_3O_2)_2H_2O$	1.88	115		gr	18.5(21.5°)
$CuSO_4 \cdot 4NH_3 \cdot H_2O$		d. 150		bl	sol. giv. $Cu(NH_3)_4^{++}$

Table of Densities, Melting Points, etc. (Cont'd)

Formula	Density	Melting Point °C	Boiling Point °C	Color	Solubility in Water
$Cu_3(AsO_4)_2 \cdot 4H_2O$				bl.–gr	v.sl.sol.
$CuHAsO_3$		d.		gr	v.sol.
CuBr	4.72	504	861–954	br	sl.sol.
$CuBr_2$		498		bl	sol.
Cu_2CO_3	4.40	d.		y	v.sl.sol.
$2CuCO_3 \cdot Cu(OH)_2$	3.88	d. 220		bl	v.sl.sol.
CuCl	3.53	422	954–1032	c	1.5(25°)
$CuCl_2 \cdot 2H_2O$	2.39	d. 110	d.	bl	43.5(20°)
$CuCl_2$	3.054	498	d.	l–y	
CuCN		high d. temp.		c	v.sl.sol.
$Cu_2Fe(CN)_6 \cdot 7H_2O$				r–br	v.sl.sol.
CuI	5.62	605	759–772	gy–br	0.0004(18°)
$Cu(NO_3)_2 \cdot 6H_2O$	2.05	26.4	d.	bl	55.6(20°)
$Cu_3(PO_4)_2 \cdot 3H_2O$				bl	sl.sol.
$CuSO_4$	3.6	200		c	
$CuSO_4 \cdot 5H_2O$	2.29	d. 20	5 aq. 230	bl	18.7(25°), 42.4(100°)
Cu_2S, Rhom.	5.6	1100		bk	
Cu_2S, Cub.	5.76	1130		bk	0.00005(18°)
CuS	4.6			bk	0.000033(18°)
CuCNS	2.85	1084		c	v.sl.sol.
Iron					
Fe	7.86	1535	3000	gy	not sol.
FeO		1420		c	v.sl.sol.
Fe_2O_3	5.12	d. 1560		r	v.sl.sol.
Fe_3O_4	5.2	d. 1538		bk	v.sl.sol.
$Fe(OH)_2$				c	0.00096(18°)
$Fe(OH)_3$	3.4–3.9	1½ aq. 500		r–br	v.sl.sol.
$FeOH(C_2H_3O_2)_2$				r	v.sl.sol.
$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$	1.86			bl–gr	25.0(25°)
FeAs	7.83	1020		w	v.sl.sol.
$FeBr_3 \cdot 6H_2O$		27		r	v.sol.
$FeBr_2$	4.64			r	6 aq. 54.3(25°)
$FeCO_3$	3.8	d.		gr–br	5.8×10^{-5}(25°)
Fe_3C	7.4	1837		gy	not sol.
$Fe(CO)_4$	2.00	d. 140		gr	v.sl.sol.
$FeCl_2 \cdot 4H_2O$	1.93			gr–w	41.5(25°)
$FeCl_3 \cdot 6H_2O$		37	280–285	r–y	47.9(20°)
$FeCl_3$	2.8	282	315	r	
$Fe_4[Fe(CN)_6]_3$		d.		bl	v.sl.sol.
$FeI_2 \cdot 4H_2O$	2.87	(an.) 177		gy	v.sol.
$Fe(NO_3)_2 \cdot 6H_2O$		35		gr–w	45.5(20°)
$Fe(NO_3)_3 \cdot 9H_2O$	1.68	47.2	d.	gy	v.sol.
Fe_2N	6.35	d.		gy	not sol.
$FeC_2O_4 \cdot 2H_2O$	2.28	d. 160		y	0.022
$Fe_2(C_2O_4)_3$		d. 100			v. sol.
Fe_3P	6.74	1100		gy	not sol.
$Fe_3(PO_4)_2 \cdot 8H_2O$	2.58			bl	v.sl.sol.
$FePO_4 \cdot 2H_2O$	2.87			y	v.sl.sol.
$FeSO_4 \cdot 7H_2O$	1.89	64	d.	bl–gr	21(20°)
$Fe_2(SO_4)_3 \cdot 9H_2O$	2.1			y	v.sol.
FeS	4.8	1193		bl	0.0006(18°)
FeS_2	5.0			y	0.0005
Fe_2S_3	4.3	d.		y–gr	v.sl.sol. giv FeS + S
$Fe(CNS)_3 \cdot 3H_2O$				r	v.sol.
Fluorine					
F_2	1.3	− 223	− 187	c	d. O_2 + HF
Gadolinium					
Gd					evol. H_2
Gd_2O_3	7.41			c	v.sl.sol.

Table of Densities, Melting Points, etc. (Cont'd)

Formula	Density	Melting Point °C	Boiling Point °C	Color	Solubility in Water
$GdCl_3$	4.62	628		c	sol.
$Gd_2(SO_4)_3$	4.14			c	8 aq. 2.4(25°)
$Gd_2(C_2O_4)_3 \cdot 10H_2O$		110		c	v.sl.sol.
Gallium					
Ga	5.91	29.75	> 1600	sil	not sol.
$GaCl_2$		175	535	c	v. sol.
$GaCl_3$	l. 2.37	75.5	217	c	v.sol.
Germanium					
Ge	5.36	958.5	2700		
GeO_2	4.70				0.40(20°)
GeH_4	l. 1.52	− 165	− 90		sl.sol.
Ge_2H_6	l. 1.98	− 109	29		sl.sol.
$GeCl_4$	l. 1.87	− 49.5	86.5		hydr.
$GeBr_4$	l. 3.13	26.1	185.9		hydr.
GeI_4	4.32	144	375		hydr.
Gold					
Au	19.3	1063	2600	y–w	not sol.
Au_2O		d. 205		v	giv. Au + Au_2O_3
Au_2O_3		d. 160		bl	v.sl.sol.
AuOH		d.		r–br	giv. Au_2O_3 + Au
$Au(OH)_3$		d. 250		y–br	v.sl.sol.
AuBr		d. 115		y–gy	v.sl.sol.
$AuBr_3$		d. 160		gy	sol.
$HAuBr_4 \cdot 5H_2O$		27		r	sol.
AuCl	7.4	d. 289.5		y	v.sl.sol.
$AuCl_3$	3.9	d. 254	s. 265	y–r	68
Au_2Cl_4	5.1	d. 250		r	d.
AuCN		d.		y	v.sl.sol.
$Au(CN)_3 \cdot 6H_2O$					v. sol.
Au_2S_2		d. 140		bk	v.sl.sol.
Au_2S_3	4.65			br	v.sl.sol.
$Au_2O_3 \cdot 2SO_3 \cdot H_2O$				y	sol.
$HAu(NO_3)_4 \cdot 3H_2O$	2.84	d. 72		y	sol.
Hafnium					
Hf		1700	> 3200	gy	not sol.
HfO_2	9.68	2812		n	v.sl.sol.
$HfOCl_2 \cdot 8H_2O$				c	sol.
K_2HfF_6				c	3.0(20°)
Helium					
He		− 268.9 (140 atm.)	− 268.9	c	0.00858 vol/vol H_2O-(20°)
Hydrogen					
H_2	0.08	− 259.1	− 252.7	c	1.93×10^{-4}(0°) 1.56×10^{-4}(25°)
HBr	l 2.16	− 86	− 67.0	c	65.9(25°)
HCl	l 1.194	− 111	− 85	c	64.2(20°), 61.6(50°)
HCN	0.699	− 14	26	c	v. sol.
HF	l 0.988	− 83	19.4	c	52.6⁻(35°)
HI	l 2.84	− 50.8	− 35.5 (4 atm.)	c	20.3 −(10°)
HN_3		− 80	37	c	sol.
H_2S	l 0.96	− 82.9	− 59.6	c	0.38(20°)
H_2Se	l 2.12	− 64	− 42	c	2.7 vol/vol H_2O(22.5°)
H_2Te	l 2.57	− 48	− 1.8	c	sol.
H_2O_2	l 1.44	− 1.7	152.1	c	v.sol.
H_2O	0.917	0	100	c	
Iodine					
I_2	4.93	113.5	184.35	pu–bk	0.0181(11°), 0.092(55°)
HIO_3	4.63	110		c	cf. I_2O_5
HIO_4			s. 110	c	v.sol.

Table of Densities, Melting Points, etc. (Cont'd)

Formula	Density	Melting Point °C	Boiling Point °C	Color	Solubility in Water
IO_2	4.21	d. 130		y	giv. $HIO_3 + I_2$
I_2O_5	4.80	d. 300		c	2 aq. 71.7(16°)
$ICl\alpha$	l 3.24	27.2	ca.97	r–br	hydr. HIO + Cl^-
$ICl\beta$	l 3.24	13.9		r–br	hydr.
ICl_3	3.11	ca.33	s.101 (16 atm.)	y	hydr.
IBr	4.41	ca. 42	ca. 116	pu–bk	hydr.
IF_5	l 3.5	8	97	c	hydr.
Indium					
In	7.3	155	1450	sil	not sol.
In_2O_3	7.18			l–y	v. sl. sol.
$InCl_2$				c	d.
$InCl_3$	4.0			c	v. sol.
InI		351		r	d.
InI_3		199		y	sol.
$In_2(SO_4)_3$	3.44			c	sol.
Iridium					
Ir	22.4	2350	4800	sil	not sol.
IrO_2				gy	v. sl. sol.
$IrCl_2$				br	v. sol.
$IrCl_3$	5.30	d. 763		d–gr	sol. if hydrated
$IrCl_4 \cdot 2NH_4Cl$	2.86	d.		d–r	0.9(27°)
$IrCl_3 \cdot 3NH_4Cl$				gr–br	sol.
$Ir_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$		106		y–r	sol.
Lanthanum					
La	6.15	826	1800	gy	$La(OH)_3 + H_2$
La_2O_3	6.51	> 2000		c	giv. sl. OH^-
$La_2(CO_3)_3 \cdot 8H_2O$				c	v. sl. sol.
$LaCl_3$	3.95	907		c	sol.
$La(IO_3)_3$				c	1.7(25°)
$La(NO_3)_3 \cdot 6H_2O$		40	126	c	60.2(25°)
$La_2(SO_4)_3 \cdot 9H_2O$	2.82	d.		c	2.91(0°), 1.86(30°)
Lead					
Pb	11.34	327.5	1620	gy	
PbO	9.53	888		y	0.002(20°)
PbO_2	9.38	d.		br	v. sl. sol.
Pb_3O_4	9.1	d. 500		r	v. sl. sol.
$Pb(OH)_2$		145		c	v. sl. sol.
$Pb(C_2H_3O_2) \cdot 3H_2O$	2.55	75	280	c	v. sol. Hydr.
$Pb_3(AsO_4)_2$	7.30	1042		c	v. sl. sol.
$Pb(C_2H_5)_4$	l. 1.66		83 (14 mm.)	c	v. sl. sol.
$Pb(BO_2)_2 \cdot H_2O$	5.60	high temp.		c	v. sl. sol.
$PbBr_2$	6.66	373	916	y	0.455(0°), 4.55(100°)
$PbCO_3$	6.6	d.315		c	0.00015(20°)
$2PbCO_3 \cdot Pb(OH)_2$		d.		l–y	v. sl. sol.
$PbCl_2$	5.85	501	950	c	0.637(0°), 3.20(100°)
$PbCl_4$	l. 3.18	− 15	d.	c	hydr. evol. Cl_2
$PbCrO_4$	6.3	844		y	0.00002(18°)
PbF_2	8.24	855	1290	c	0.068(27°)
PbI_2	6.16	402	954	y	0.044(0°), 0.434(100°)
$Pb(IO_3)_2$		d. 300		c	0.003(25°)
$Pb(NO_3)_2$	4.53	470		c	34.3(20°)
PbC_2O_4	5.28	d. 300		c	0.00015(18°)
$PbCl_2 \cdot PbO$	7.21	d. 524		c	v. sl. sol.
$Pb_3(PO_4)_2$	6.9–7.3	1014		c	0.000014(20°)
$Pb(PO_3)_2$		800		c	c. sl. sol.
PbS	7.5	1114		bk.	2.9×10^{-5}(18°)
$PbSO_3$				c	v. sl. sol.

Table of Densities, Melting Points, etc. (Cont'd)

Formula	Density	Melting Point °C	Boiling Point °C	Color	Solubility in Water
$PbSO_4$	6.2	1170		c	0.0042(20°)
$Pb_2O(SO_4)$	6.92	977		c	v. sl. sol.
$Pb(CNS)_2$	3.82			y	0.5(20°)
$PbSiO_3$	6.49	766		□	v. sl. sol.
Lithium					
Li	0.53	186	1200	gy	giv. $LiOH + H_2$
Li_2O	2.01	> 1700		c	giv. LiOH
LiOH	2.54	450		c	11.3(10°), 14.9(100°)
$LiC_2H_3O_2 \cdot 2H_2O$		70	d.	c	300(15°)
$LiHCO_3$				c	5.5(13°)
LiBr	3.46	547	1265	c	2 aq. 66.2(34°)
Li_2CO_3	2.11	618		c	1.51(0°), 0.725(100°)
LiCl	2.07	613	1353	c	1 aq. 45.9(25°)
$LiClO_4$	2.43	236	d.410	c	37.4(25°)
LiF	2.30	870	1670	c	0.26(18°)
LiH	0.82	680		□	giv. $LiOH + H_2$
LiI					3 aq. 62(20°)
$LiNH_2$	1.18	390		□	hydr.
$LiNO_3$	1.77	255		c	3 aq. 42.9(22°)
Li_3PO_4	2.54	837		c	0.04
Li_2S	1.66			c	v. sol.
Li_2SO_4	2.22	860		c	1 aq. 25.7(20°)
$Li_2O \cdot SiO_2$	2.33	1201		c	sol.
Magnesium					
Mg	1.74	651	1110	w	giv. $Mg(OH)_2 + H_2$
MgO	3.65	2800		c	giv. $Mh(OH)_2$ slowly
$Mg(OH)_2$	2.36	d.		□	0.0009(18°)
$Mg(C_2H_3O_2)_24H_2O$	1.45			c	v. sol.
$MgNH_4AsO_4 \cdot 6H_2O$	1.93	d.		c	0.021(20°)
$MgNH_4PO_4 \cdot 6H_2O$	1.72	d.		c	0.04(20°)
$MgBr_2 \cdot 6H_2O$	anh. 3.72	anh. 700		c	49.1(20°)
$MgCO_3$	3.08	d.450		c	0.01(18°) hydr.
$4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$	2.18			c	v. sl. sol.
$MgCl_2 \cdot 6H_2O$	1.56	d.118		c	35.3(20°)
MgF_2	3.0	1396		c	0.009(20°)
MgI_2	4.25	d.		c	8 aq. 59.7(18°)
$Mg(NO_3)_2 \cdot 6H_2O$	1.46	95	5 aq. 330	c	43.1(18°)
$MgC_2O_4 \cdot 2H_2O$		d.		c	0.03(18°)
$MgHPO_4 \cdot 3H_2O$				c	0.3
$Mg_2P_2O_7$	2.60			c	v. sl. sol.
$MgSO_4$	2.66	1185		□	
$MgSO_4 \cdot 7H_2O$	1.68	d.		c	26.8(25°)
MgS	2.8	d.		gy	hydr.
Manganese					
Mn	7.2	1260	1900	gy–pk	giv. $Mn(OH)_2 + H_2$
Mn_2O_7		< − 20	exp.		v. sol.
MnO	5.18	1650		gy–gr	v. sl. sol.
Mn_2O_3	4.50			bk	v. sl. sol.
MnO_2	5.02			bk	v. sl. sol.
Mn_3O_4	4.7	v. high		bk	v. sl. sol.
$Mn(OH)_2$	3.26	d.		l–pk	0.00019(18°)
$Mn_2O_3 \cdot H_2O$	3.26	d.		br	v. sl. sol.
$Mn(C_2H_3O_2) \cdot 4H_2O$	1.59			l–r	3
$NH_4MnPO_4 \cdot 7H_2O$				c	0.003
$MnBr_2$	4.38			ro–r	4 aq. 58.8(20°)
$MnCO_3$	3.12	d.		ro	0.0065(25°)
$MnCl_2$	2.98	650	1190	pk	
$MnCl_2 \cdot 4H_2O$	2.01	58.01	106	r–or	43.6(25°)
MnF_2	3.98	856		ro	sol.

Table of Densities, Melting Points, etc. (Cont'd)

Formula	Density	Melting Point °C	Boiling Point °C	Color	Solubility in Water
MnF_3	3.54			r	hydr.
$MnI_2 \cdot 4H_2O$		d.		ro	v. sol.
$Mn(NO_3)_2 \cdot 6H_2O$	1.82	25.8	129.4	ro	63(25°)
$MnC_2O_4 \cdot 2\frac{1}{2}H_2O$	2.43	d. 150		pk–ro	0.03(25°)
$Mn_3(PO_4)_2 \cdot 7H_2O$				ro	sl. sol.
$Mn_2P_2O_7$	3.71			ro	sl. sol.
$MnSiO_3$	3.48	1273		r	v. sl. sol.
MnS	3.99	d.		l–ro	0.00047(18°)
MnS_2	3.46			r	d.
$MnSO_4$	3.25	700		r	
$MnSO_4 \cdot 5H_2O$	2.11	d.		ro	39.3(25°)
Mercury					
Hg	14.19	− 38.87	356.9	sil.	not sol.
Hg_4O_2	9.8	d. 100		bk	v. sl. sol.
HgO	11.14	d. 100	d.	y and r	0.00515(25°)
$Hg(C_2H_3O_2)_4$	3.27	d.		c	25 g./100 g. H_2O(25°)
$Hg_3(AsO_4)_2$				y	sl. sol.
Hg_2Br_2	7.31		s. 345	y	3.9×10^{-6}(25°)
$HgBr_2$	6.05	237	322	l–y	0.6(25°)
$Hg_4(CO_3)_2$		d. 130		y	v. sl. sol.
Hg_2Cl_2	7.15	302	383.7	c	0.0003(25°)
$HgCl_2$	5.44	277	304	c	6.89(25°), 35.1(100°)
$Hg_4(CrO_4)_2$		d.		r	sl. sol.
$Hg(CN)_2$	4.00	d.		c	9.3(20°)
Hg_2F_2	8.73	570		c	sol.
HgF_2	8.95	d. 645	851	c	sol.
Hg_2I_2	7.70	d. 290	d.	y	2×10^{-8}(25°)
HgI_2	6.28	Tr. 127		r	0.004(17.5°)
HgI_2	6.27	259	354	y	v. sl. sol.
$Hg_2(NO_3)_2 2H_2O$	4.78	70		c	sol.
$Hg_2(NO_2)_2$	5.92	d. 140		c	sl. sol.
$NHg_2Br \cdot 3NH_4Br$		d. 180		c	v. sl. sol.
$Hg_3(PO_4)_2$				c	v. sl. sol.
$Hg_3(PO_4)_2$				w to y	v. sl. sol.
Hg_2S		d. 0°		bk	v. sl. sol.
HgS	α8.1 β7.7	s. 580		bk	1×10^{-6}(18°)
$Hg_2(SO_4)$	7.56	d.	d.	c	0.06(25°)
$HgSO_4$	6.47	d.		c	
$HgSO_4 \cdot 2H_2O$	6.44			y	hydr. to basic salt
Molybdenum					
Mo	10.2	2620	3700	gy	not sol.
$MoO_3 \cdot 2H_2O$	3.12			y	0.18(23°), 1.70(70°)
MoO_2	4.52			r	v. sl. sol.
Mo_2O_3				y to bl	v. sl. sol.
MoO_3	4.50	795	s.	y	0.107(18°), 1.705(70°)
$MoCl_2$		d.		y	v. sl. sol.
$MoCl_3$		d.		w	v. sl. sol.
$MoCl_4$				br	v. sol.
$MoCl_5$		194	268	bl	v. sol.
MoF_6		17	35	c	hydr.
$MoOF_4$	3.0	98	180	c	sol.
MoI_2	4.3			br	v. sl. sol.
MoS_2	4.8	1185		bl	v. sl. sol.
Mo_2S_3	5.91			gy	v. sl. sol.
MoS_3		d.		r–br	sl. sol.
Neon					
Ne	1.0	− 248.67	− 245.9	c	1.5 cc./100 cc. H_2O(20°)

Table of Densities, Melting Points, etc. (Cont'd)

Formula	Density	Melting Point °C	Boiling Point °C	Color	Solubility in Water
Nickel					
Ni	8.9	1452	2900	sil.	not sol.
NiO	7.45			gr	v. sl. sol.
$Ni_3O_4 \cdot 2H_2O$	3.41			gy	v. sl. sol.
$NiO_2 \cdot xH_2O$		d.		bk	v. sl. sol.
$Ni(OH)_2$	4.36			gr	0.0013
$Ni(C_2H_3O_2)_2$	1.80	d.		gr	sol.
$NiCl_2NH_4Cl \cdot 6H_2O$	1.64			gr	v. sol.
$NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	1.92			gr	25(3.5°)
$Ni_3(AsO_4)_2$	4.98			gr	v. sl. sol.
$NiBr_2$	4.64	d.		y	6 aq. 57.3(25°)
$NiCO_3$		d.		l–gr	v. sl. sol.
$2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$		d.		l–gr	v. sl. sol.
$Ni(CO)_4$	l. 1.31	− 25	43	c	0.018(9.8°)
$NiCl_2$	3.54		973	y	53.8(0°), 87.6(100°)
$NiCl_2 \cdot 6H_2O$				gr	39.0(20°)
$Ni(ClO_3)_2 \cdot 6H_2O$	2.07	d. 80		d–r	0.9(27°)
$Ni(ClO_3)_2 \cdot 6NH_3$	1.52	180			giv. $Ni(NH_3)_4^{++}$
$Ni(CN)_2 \cdot 4H_2O$		4 aq. 200		gr	sol.
NiI_2		s.		bl	6 aq. 59.7(20°)
$Ni(NO_3)_2 \cdot 6H_2O$	2.05	56.7	136.7	gr	238.5(0°)
Ni_2P	6.31	1112		gy	not sol. sol. HNO_3
$Ni(H_2PO_2)_2 \cdot 6H_2O$	1.82	d.		gr	sol.
$Ni_3(PO_4)_2 \cdot 7H_2O$				gr	v. sl. sol.
NiS	4.6	797		bk	0.00036(18°)
$NiSO_4$	3.68			y	
$NiSO_4 \cdot 7H_2O$	1.948	99		gr	25.5(15°)
Nitrogen					
N_2	1.03	− 209.86	− 195.8	c	0.0019(20°)
HNO_3	l. 1.502	− 42	86	c	v. sol.
NO	l. 1.27	− 161	− 151.0	c	0.0056(25°)
NO_2	l. 1.45	− 9.3	21.3	y–br	giv. $HNO_2 + HNO_3$
N_2O	l. 1.23	− 102.4	− 89.5	c	0.121(20°)
N_2O_3	l. 1.45	− 102	3.5	bl	giv. HNO_2
N_2O_5		30	47	c	giv. HNO_3
$NH_2 \cdot NH_2$	l. 1.01	1.4	113.5	c	v. sol.
$N_2H_4H_2O$	l. 1.03	< − 40	118.5	c	v. sol.
$N_2H_4 \cdot 2HNO_3$		104		c	v. sol.
$N_2H_4 \cdot HCl$		89		c	sol.
$N_2H_4 \cdot 2HCl$	1.42	198		c	sol.
$N_2H_4HClO_3$		exp. 80		c	sol.
$N_2H_4H_2SO_4$	1.37	254		c	3.0(22°)
NH_2OH	1.35	34	56.5	c	sol. H_2O + alcohol
$NH_2OH \cdot HCl$	1.67	151		c	sol.
$(NH_2OH)_2H_2SO_4$		170		c	sol.
N_3H		− 80	37	c	sol.
NH_2NO_2		d. 72		c	hydr.
NOF		− 134	− 56	c	gw. $HNO_2 + HF$
NCl_3	l. 1.65		< 71	y	hydr.
NOCl	l. 1.41	− 64.5	− 5.5	y–r	sl. sol.
NOBr		− 55.5	− 2	d–br	hydr.
$NOBr_3$	l. 2.64	− 40	ca. 32	br	hydr.
NH_3I_2	l. 2.46	− 2	d. 15	d–br	v. sl. sol.
NI_3NH_3	3.5	d. > 20		d–br	v. sl. sol.
N_2S_5	l. 1.90	11		r	d.
N_4S_4	2.22	178	s. 135	y–r	giv. NH_3, SO_2, $H_2S_2O_6$
$N_2O_3 \cdot 2SO_3$	2.14	230	357.3	c	hydr.
NO_2SO_3H		d. 73		c	hydr.

Table of Densities, Melting Points, etc. (Cont'd)

Formula	Density	Melting Point °C	Boiling Point °C	Color	Solubility in Water
$SO_2(NH_2)_2$		92		c	hydr.
NH_2SO_3H	2.03	d. 205		c	hydr.
$NH(SO_3NH_4)_2$	1.96	357		c	giv. $(NH_4)_2SO_4$
Osmium					
Os	22.48	2700	> 5300	bl.	not sol.
OsO_2	7.9			bl–r	v. sl. sol.
OsO_4	4.91	41	134	y	5.8(15°)
OsO_4		39.5		c	
$OsCl_2$				gr	sl. sol.
$OsCl_3$				br	sl. sol.
$OsCl_4$				r to y	sl. sol.
OsF_6			203		hydr.
OsF_3		34.5	47.3	c	giv. OsO_4
OsS_2				y	sl. sol.
OsS_4		d.		bl	not sol.
Oxygen					
O_2	1.43	− 218.4	− 183.0	l–bl	0.00434(20°), 0.00079-(90°)
O_3		− 251.4	− 112	bl	0.0026(15°)
Palladium					
Pd	12.0	1555	2200	sil	not sol.
PdO		d. 877		bk	v. sl. sol.
PdO_2				bk	v. sl. sol.
$Pd(OH)_2$				br	v. sl. vol.
$PdBr_2$				br	v. sl. sol.
$PdCl_2$		500		d–br	sl. sol.
PdI_2		d. 350		bk	v. sl. sol.
$Pd(NO_3)_2$		d.		y	sol.
PdS		950		bk	v. sl. sol.
Pd_2S	7.3	d. 800		gr	
PdS_2		d.		br	v. sl. sol.
$PdSO_4 \cdot 2H_2O$				br	v. sol.
$(NH_4)_2PdCl_4$	2.17			y–gr	sol.
$(NH_4)_2PdCl_6$	2.42			r	sl. sol.
$Pd(CO)_2Cl_2$		1.42		y–r	d.
Phosphorus					
P_4 yellow	1.82	44.1	280	y	0.0003(15°)
P_4 red	2.20	590 (43 atm.)	280	r	v. sl. sol.
P_2O_3	2.13	22.5	90(300)	c	giv. H_3PO_3
P_2O_4	2.53	> 100	s. ca. 180	c	giv. H_3PO_3
P_2O_5	2.39	ca. 563	s. 347	c	giv. H_3PO_4
H_3PO_3	1.65	73.6	d. 200	y	v. sol.
H_3PO_2	1.49		d.	c	v. sol.
H_3PO_4	1.83	42.35	d.	c	86(24°)
HPO_3	2.2–2.5	sub. at w. heat		c	sol.
$H_4P_2O_7$		61		c	89(23°)
PBr_3	l. 2.85	− 40	172.9		hydr.
PBr_5			106	y	hydr.
PCl_3	l. 1.57	− 111.8	73.5	c	hydr.
PCl_5		148	162	l–y	hydr.
P_2Cl_4		− 28	180	c	hydr.
$POCl_3$	l. 1.67	1.25	107.23	c	hydr.
PH_4Cl		28 (46 atm.)		c	sol.
PF_3	3.02	− 160	− 95	c	hydr.
PF_5	4.49	− 83	− 75	c	hydr.
POF_3	3.63	− 68	− 40	c	hydr.
PH_3	l. 0.75	− 132.5	− 87.4	c	sl. sol.
P_2H_4	l. 1.01	< − 10	57.5 (735 mm.	c	v. sl. sol.
$P_{12}H_6$	1.83			y	v. sl. sol.

Table of Densities, Melting Points, etc. (Cont'd)

Formula	Density	Melting Point °C	Boiling Point °C	Color	Solubility in Water
PI_3		61		r	hydr.
P_2I_4		110		r	hydr.
PH_4I			s. 61.8 (708)	c	sol.
P_2S_3		290	490	gy–y	d.
P_2S_5	2.03	276	514	gy–y	d.
P_4S_3	2.03	172.5	407.5	y	not. sol. d. by hot water
$PSBr_3$	2.85	38.0			hydr.
Platinum					
Pt	21.45	1755	4300	sil–gy	not sol.
PtO		555		v–bk	v. sl. sol.
PtO_2		430		bk	v. sl. sol.
$Pt(OH)_2$		d.		bk	v. sl. sol.
$Pt(OH)_4$		d.		r–br	v. sl. sol.
$PtBr_2$		d. 300		br	v. sl. sol.
$PtBr_4$		d. 180			0.41(20°)
$PtCl_2$	5.87	d. 581		gr–gy	v. sl. sol.
$PtCl_4 \cdot 8H_2O$	2.43	d.		r	v. sol.
$Pt(CO)Cl_2$		195	s. 240	y	giv. CO_2, HCl & Pt
$H_2PtCl_6 \cdot H_2O$	2.43	d.		r–br	sol.
PtI_2		d. 325		bk	v. sl. sol.
PtI_4		d. 100		br–bk	sol.
PtP_2O_7	4.85	d. > 600		gr–y	v. sl. sol.
PtS	8.90	d.		bk	v. sl. sol.
PtS_2	5.27	d.		y–br	v. sl. sol.
$Pt(SO_4)_2 \cdot 4H_2O$				y	sol.
Potassium					
K	0.86	62.3	760	sil	giv. KOH + H_2
K_2O	2.32			gy	giv. KOH
K_2O_4		> 280		y	giv. KOH + H_2O_2 + O_2
KH	0.80	d.		c	giv. KOH + H_2
KOH	2.04	380	1320	c	2 aq. 53(22°) 1 aq. 66-(110°)
$KC_2H_3O_2$	1.8	292		c	255 g./100 g. H_2O(20°)
$K_2Al_2O_4 \cdot 3H_2O$				c	sol.
$KSbO_3$				c	sl. sol.
$KSbOC_4H_4O_6 \cdot \frac{1}{2}H_2O$	2.61			c	7.85(25°)
K_3AsO_4				c	sol.
KH_2AsO_4	2.87	288		c	15.9(6°)
$KAsO_2$				c	sol.
K_2AuCl_4		357		y	38.2(20°)
$K_2B_4O_7 \cdot 5H_2O$		5 aq. red heat		c	sol. hydr. sl.
$KBrO_3$	3.27	d. 370		c	3.1(0°), 11.7(40°)
KBr	2.75	730	1380	c	39.4(20°), 51.2(100°)
K_2PtBr_6	4.66	d. > 400			2.0(20°)
K_2CO_3	2.29	891		c	2 aq. 53(25°)
$KHCO_3$	2.17	d.		c	18.3(0°), 28.1(30°)
KCl	1.99		1416	c	22.0(0°), 25.8(25°)
KClO		d.		c	v. sol.
$KClO_3$	2.32	368.4		c	3.2(0°), 9.2(30°)
$KClO_4$	2.52	d. 400		c	0.7(0°), 15.8(100°)
K_2PtCl_6	3.50	d. 250		y	0.5(0°), 5(100°)
K_2CrO_4	2.73	975		y	38.6(20°)
$K_2Cr_2O_7$	2.69	398		r	4.7(0°), 50.5(100°)
$K_3Co(NO_2)_6 \cdot {}^3/_2H_2O$		d. 200		y	0.09(0°)
KCN	1.52	634.5		c	v. sol.
KCNO	2.05			c	sol.
$KAg(CN)_2$				c	12.5
$K_3Fe(CN)_6$	1.89			r	29.0(15.6°)
$K_4Fe(CN)_6 \cdot 3H_2O$	1.85	3 aq. 70		y	19.7(20°), 39(75°)

Table of Densities, Melting Points, etc. (Cont'd)

Formula	Density	Melting Point °C	Boiling Point °C	Color	Solubility in Water
KF	2.48	880	1500	c	2 aq. 49(21°)
KBF_4	2.50	d. 500		c	sol.
$3KF \cdot AlF_3$		1035		c	sol.
K_2SiF_6	2.66			c	0.12(17.5°), 0.95(100°)
KI	3.12	773	1330	c	59.0(20°)
KI_3	3.50	45	d. 225	br	sol.
KIO_3	3.89	560		c	7.5(20°)
KIO_4	3.62	582		c	0.66(13°)
K_2MnO_4		d. 190		d–gr	sol.
$KMnO_4$	2.70	d. < 240		pu	7.1(25°), 20(65°)
K_2MoO_4	l. 2.34	919		c	v. sol.
KNO_3	1.91	297	d. 350	c	75.8(25°)
KNO_2	2.11	333	d. 400	c	24.0(20°), 71(100°)
KNH_2		338		c	hydr.
$K_2C_2O_4 \cdot H_2O$	2.13			c	27.4(25°)
K_3PO_4		1340		c	sl. sol.
K_2HPO_4		d.		c	v. sol.
KH_2PO_4	2.34	d. 256		c	25 g./100 g. H_2O(7°)
$K_4P_2O_7$	2.33	1090		c	sol.
K_2HPO_3		d.		c	v. sol.
K_2SiO_3		976		c	sol.
K_2SeO_4	3.07			c	52.6(18°)
K_2S	1.80	471		br	sol. hydr.
K_2S_5		206		y	v. sol.
$K_2SO_3 \cdot 2H_2O$		d.		c	v. sol.
$KHSO_4$	2.35	210		c	v. sol.
K_2SO_4	2.66	1067		c	10.75(25°), 19.4(100°)
$K_2S_2O_7$	2.28	> 300		c	sol.
$K_2S_2O_8$		d. < 100		c	1.6(0°), 5.0(20°)
KCNS	1.89	173.2		c	v. sol.
$K_2C_4H_4O_6 \cdot \frac{1}{2}H_2O$	1.98			c	59(17°)
K_2WO_4	3.12	921		c	sol.
Praseodymium					
Pr	6.5	940		gy	evol. H_2
Pr_2O_3	6.87			y–gr	sl. sol.
$PrCl_3$	4.02	818		gr	51(13°)
Pr_2S_3	5.04			br	d.
$Pr_2(SO_4)_3$	3.72			gr	8 aq. 12.4(18°)
Radium					
Ra	5	960	1140	sil	evol. H_2
$RaBr_2$	5.79	7.28		y	sol.
$RaCl_2$	4.91	1000		y	sol.
Rhodium					
Rh	12.5	1995	> 2500	gy–w	not sol.
RhO				gy	v. sl. sol.
Rh_2O_3				gy	v. sl. sol.
RhO_2				br	v. sl. sol.
$Rh(OH)_3$		d.		bk	v. sl. sol.
$RhCl_3$		d. 475		r	sol. if hydrated
$Rh(NO_3)_3 \cdot 2H_2O$				r	sol.
$Rh_2(SO_4)_3 \cdot 12H_2O$				l–y	v. sol.
RhS		d.		bl	v. sl. sol.
Rubidium					
Rb	1.53	38.5	700	sil	giv. $RbOH + H_2$
Rb_2O	3.72	d. 400		c	giv. RbOH
Rb_2O_2	3.65			y	giv. $RbOH + H_2O_2$
Rb_2O_4	3.05	280		y	giv. $ROH + H_2O_2 + O_2$
RbOH	3.20	300		gy	36.4(30°)
RbBr	3.35	682	1340	c	51.2(16°)
Rb_2CO_3		837		c	v. sol.

Table of Densities, Melting Points, etc. (Cont'd)

Formula	Density	Melting Point °C	Boiling Point °C	Color	Solubility in Water
RbCl	2.76	715	1390	c	47.7(20°)
RbF	l. 2.88	760	1410	c	sol.
RbI	l. 2.87	642	1300	c	60(17°)
$RbNO_3$	l. 2.39	310		c	34.8(20°)
Rb_2S	2.91			c	v. sol.
Rb_2SO_4	3.61	1060		c	32.5(20°)
Ruthenium					
Ru	12.2	2450	> 2700	gy	not sol.
Ru_2O_3				bl–bk	v. sl. sol.
RuO_2	7.2			v	v. sl.
RuO_4	5.77	25.5	100.8 183 mm.	y	sl. sol.
$Ru(OH)_3$				bk	v. sl. sol.
$RuCl_3$				br	sol.
RuS_2				bk	v. sl. sol.
RuSi	5.4			w	v. sl. sol.
Scandium					
Sc	2.5	1200	2400	sil	evol. H_2
Sc_2O_3	3.86			c	v. sl. sol.
$ScCl_3$		939		c	v. sol.
$Sc(NO_3)_3$		150		c	sol.
$Sc_2(SO_4)_3$	2.58			c	5 aq. 28.5(25°)
Selenium					
Se_8	4.5–4.8	220	688	gy	not sol.
H_2SeO_3	3.00	d.		c	62.5(20°)
H_2SeO_4	2.95	58		c	v. sol.
SeO_2	3.95	340	s. 317	c	giv. H_2SeO_3
Silicon					
Si	2.4	1420	2600	gy	not sol.
H_2SiO_3	1.81			c	sl. sol.
H_4SiO_4	1.57			c	sl. sol.
SiO_2, quartz	2.65	cristobalite 1710		c	v. sl. sol.
SiO_2, glass	2.20		2230	c	v. sl. sol.
$SiBr_4$	2.81	5	153		hydr.
SiC	3.17	> 2700	s. 2210 diss.		v. sl. sol.
$SiCl_4$	l. 1.48	− 70	57	y	hydr.
SiF_4		− 77	− 65 at (1801 mm.)		hydr.
SiH_4	l. 0.68 (− 185)	− 185	− 112	c	sl. sol.
Si_2H_6	l. 0.69 (−25)	− 132.5	− 15	c	sl. sol.
Si_3H_8	l. 0.725 (0)	− 117	53	c	sl. sol.
Si_4H_{10}	l. 0.79 (0)	− 93.5	80	c	sl. sol.
SiI_4		120.5	290	c	hydr.
Silver					
Ag	10.5	960.5	1950	sil	not sol.
Ag_2O	7.14	d. 300		br	0.00215(20°)
Ag_2O_2	7.44	d. > 100		bk	v. sl. sol.
$AgC_2H_3O_2$	3.26	d.		gr	1.021(20°), 2.52(80°)
Ag_3AsO_3		d. 150		y	0.00115(20°)
Ag_3AsO_4	6.66			d–r	0.00085(20°)
AgBr	6.47	434		l–y	0.000013(25°)
$AgBrO_3$	5.21	d.		c	0.159(20°)
Ag_2CO_3	6.08	d. 218		c	0.002
$AgClO_3$	4.43	230		c	sol.

Table of Densities, Melting Points, etc. (Cont'd)

Formula	Density	Melting Point °C	Boiling Point °C	Color	Solubility in Water
$AgClO_4$		d. 486		c	84(25°)
AgCl	5.56	455	1550	c	0.00015(20°)
$2AgCl \cdot 3NH_3$		d. 68		c	giv. $Ag(NH_3)_2^+$
Ag_2CrO_4				d–r	0.0025(18°)
$Ag_2Cr_2O_7$		d.		r	0.0083(15°)
AgCN	3.95	d. 320		c	0.00002(25°)
AgCNO	4.00	d.		c	0.003(18)
$Ag_3Fe(CN)_6$				or	0.00007(20°)
$Ag_4Fe(CN)_6 \cdot H_2O$				c	v. sl. sol.
$AgNO_2$	4.45	d. 140		c	0.4(25°)
AgF	5.85	435		y	4 aq. 57.5(15°)
AgI	5.67	d. 552		y	2.5×10^{-7}(25°)
$AgIO_3$	5.52	> 200		c	0.0038(18°)
AgN_3		exp. 251.5		bk	v. sl. sol.
$AgNO_3$	4.35	212	d. 444	c	68.3(20°)
$Ag_2C_2O_4$	5.03	ex. 140		c	0.004(25°)
$AgMnO_4$		d.		bl–bk	1.5(25°)
Ag_2P_3	4.63	d.		gy	v. sl. sol.
$AgPO_3$	6.37	482			v. sl. sol.
Ag_3PO_4	6.37	849		l–y	0.0006(25°)
$Ag_4P_2O_7$	5.31	585		c	v. sl. sol.
Ag_2S	7.32	825		bk	1×10^{-5}
Ag_2SO_3		d. 100		c	sl. sol.
Ag_2SO_4	5.45	652		c	0.8(25°)
AgCNS				c	0.00002(25°)
Sodium					
Na	0.97	97.5	880	sil	giv. NaOH & H_2
Na_2O	2.27			gy	giv. NaOH
Na_2O_2		d. 30		y–w	giv. NaOH & HO_2^-
NaOH	2.13	318.4	1390	c	1 aq. 51.7(25°)
$NaC_2H_3O_2$	1.53	324		c	46 g./100 g. H_2O(20°)
$NaAlO_2$		1650		c	sol.
$2NaSbO_3 \cdot 7H_2O$				c	0.03(12°)
$Na_2H_2Sb_2O_7 \cdot H_2O$				c	sl. sol.
$Na_3AsO_4 \cdot 12H_2O$	1.80	86.3		c	10.4(17°)
$Na_2HAsO_4 \cdot 12H_2O$	1.72	28		c	27(21°)
Na_2HAsO_3	1.87			c	v. sol.
$NaBO_2$		966	> 1400	c	sol.
$Na_2B_4O_7 \cdot 10H_2O$	1.73	75		c	1.6(10°) 5 aq. 34(100°)
NaBr	3.20	755	1390	c	2 aq. 47.5(20°)
$NaBrO_3$	3.34	381		c	27.7(20°)
Na_2CO_3	2.53	851		c	
$Na_2CO_3 \cdot H_2O$	1.55			c	31(100°)
$Na_2CO_3 \cdot 10H_2O$	1.46			c	23.0(25°)
$NaHCO_3$	2.20			c	8.8(20°)
$NaClO_3$	2.49	248		c	50(20°)
$NaClO_4$		482		c	sol.
NaCl	2.16	804	1413	c	26.4(20°), 28.2(100°)
$NaClO \cdot 2.5H_2O$		57.5		c	v. sol.
$Na_2PtCl_4 \cdot 4H_2O$		d. 100		r	sol.
$Na_2PtCl_6 \cdot 6H_2O$	2.50			r	sol.
$Na_2CrO_4 \cdot 10H_2O$	1.48			y	33.4(10°)
$Na_2Cr_2O_7 \cdot 2H_2O$	2.52	320		r	64.3(20°)
NaCN		563.7	1496	c	v. sol.
$NaCu(CN)_2$	1.01	d. 100		c	sol.
$Na_3Fe(CN)_6H_2O$				r	sol.
$Na_4Fe(CN)_6 \cdot 10H_2O$	1.46			y	20.7(25°)
$Na_2Fe(CN)_5NO$ $\cdot 2H_2O$	1.72			r	v. sol.
Na_2CbO_3	4.19			l–y	sol.

Table of Densities, Melting Points, etc. (Cont'd)

Formula	Density	Melting Point °C	Boiling Point °C	Color	Solubility in Water
NaF	2.79	980	1700	c	4.3⁻(18°)
$3NaF \cdot AlF_3$	2.90	1000		c	sol.
Na_2SiF_6	2.68			c	0.65(17.5°), 2.4(100°)
$NaCHO_2$	1.92	253		c	46.9(21°)
NaH	0.92			c	giv. $NaOH + H_2$
NaI	3.67	651	1300	c	2 aq. 64.8(25°)
$NaIO_3$	4.27	d.		c	2.4(0°), 25.3(100°)
$Na_2MnO_4 \cdot 10H_2O$		d.		gr	v. sol.
Na_2MoO_4	l. 2.59	687		pu	2 aq. 39.4(20°)
$NaNH_2$		210		c	hydr.
$NaNO_2$	2.17	271		c	44.9(15°)
$NaNO_3$	2.57	308		c	46.8(20°)
$Na_2C_2O_4$				c	3.1(15°), 4.3(50°)
$NaH_2PO_2 \cdot H_2O$				c	sol.
$Na_2HPO_3 \cdot 5H_2O$				c	sol.
$NaPO_3$	2.48	d. 616		c	sl. sol.
$NaH_2PO_4 \cdot H_2O$	2.07	d. 190		c	2 aq. 48(25°)
$Na_2HPO_4 \cdot 12H_2O$	1.52	34.6		c	11(25°)
$Na_3PO_4 \cdot 12H_2O$	1.62	d. 73.4		c	9.5(15°)
$Na_4P_2O_7 \cdot 10H_2O$	1.82	d.		c	3.1(0°), 23.1(80°)
$NaKCO_3 \cdot 6H_2O$	1.63	6 aq. 100		c	v. sol.
$NaC_7H_5O_3$				c	36(25°)
Na_2SeO_4	3.10			c	10 aq. 30.3(20°)
Na_2SiO_3		1088		c	v. sol.
$Na_2Si_4O_9$				c	v. sol.
$Na_2SnO_3 \cdot 3H_2O$				c	37(20°)
Na_2S	1.85			y	9 aq. 16.2(22°)
Na_2S_5		251.8		y	v. sol.
Na_2SO_3	1.56			c	7 aq. 20.1(18°)
$Na_2S_2O_3 \cdot 5H_2O$	1.68	d. 48.0		c	41.2(20°), 2 aq. 73-(100°)
$NaHSO_4$	2.74	> 315		c	v. sol.
Na_2SO_4	2.69	884		c	29.9(100°)
$Na_2SO_4 \cdot 10H_2O$	1.46	d. 324		c	16.1(20°)
$NaCNS$		562.3		c	v. sol.
$Na_2C_4H_4O_6 \cdot 2H_2O$	1.82			c	v. sol.
Na_3VO_4		ca. 866		c	sol.
Na_2WO_4	4.18	698		c	2 aq. 42.2(20°)
Strontium					
Sr	2.6	800	1150	sil	giv. $Sr(OH)_2 + H_2$
SrO	4.7			gy–w	giv. $Sr(OH)_2$
$Sr(OH)_2$	3.62			c	8 aq. 0.4(0°), 21.8(100°)
$SrBr_2$	4.22	643		c	
$SrBr_2 \cdot 6H_2O$	2.36	d. 20		c	50.0(20°)
$SrCO_3$	3.70	1497 (60 atm.)		c	0.001(18°)
$SrCl_2$	3.05	873		c	
$SrCl_2 \cdot 6H_2O$	1.93	d. 61		c	35.0(20°), 45.4(60°)
$Sr(ClO_3)_2$	3.15	d. 120		c	63.6(18°)
$SrCrO_4$	3.89			y	0.11(15°)
SrF_2	2.44	1190		c	0.0017(18°)
SrI_2	4.54	402		c	
$SrI_2 \cdot 6H_2O$	4.41			c	64.2(20°)
$Sr(NO_3)_2$	2.99	570		c	50.3(100°)
$Sr(NO_2)_2 \cdot 4H_2O$	2.2			c	41.5(20°)
$SrC_2O_4 \cdot H_2O$		d.		c	0.006(20°)
$SrHPO_4$	3.54			c	v. sl. sol.
SrS	3.70			c	sol. hydr.
$SrSO_3$		d.		c	sl. sol.
$SrSO_4$	3.96	d. 1580		c	0.01(20°)
$SrSiO_3$	3.65	1580		c	v. sl. sol.

Table of Densities, Melting Points, etc. (Cont'd)

Formula	Density	Melting Point °C	Boiling Point °C	Color	Solubility in Water
Sulfur					
S(M)	1.96	119.0	444.6	y	not sol.
S(R)	2.07	112.8	444.6	y	not sol.
SO_2		− 72.7	− 10	c	10.0(20°), 4.5(50°)
SO_3	l. 1.92	16.83	44.6	c	g. H_2SO_4
H_2SO_4	l. 1.83	10.49		c	v. sol.
$H_2SO_4 \cdot H_2O$	l. 1.84	8.62	290	c	v. sol.
$H_2SO_4 \cdot 2H_2O$	l. 1.65	− 38.9	167	c	v. sol.
$H_2S_2O_7$	l. 1.9	35.0	d.	c	g. H_2SO_4
$SOBr_2$	l. 2.68	− 50	68	or–r	giv. $SO_2 + HCl$
SOClBr	l. 2.31		115 d.	y	d.
SCl_4		− 30		y–br	d.
S_2Cl_2	l. 1.67	− 80	138	y–r	giv. $HCl + S + H_2S_2O_3$ slowly
$SOCl_2$	l. 1.63		78.8	d–y	giv. $SO_2 + HCl$
SO_2Cl_2	l. 1.66	− 54.1	69.1	c	sl. sol. 0°, d. by hot H_2O
$SO_2SO_2Cl_2$	l. 1.84	− 37.5	153	c	giv. $H_2SO_4 + HCl$ slowly
$S_2O_5Cl_4$	0	d. 57		w	d.
SF_6		− 55		c	sl. sol. hot d.
SOF_2		− 110	− 30	c	giv. $SO_2 + HF$
SO_2F_2		− 120(65 mm.)	− 52	c	10 vol./100 vol. H_2O(9°)
Tantalum					
Ta	16.6	2770	> 4100	gy	not sol.
Ta_2O_5	8.73	d. 1470		c	v. sl. sol.
$TaBr_5$		240	320	y	sol. hydr.
$TaCl_5$	3.68	221	242	y	sol. hydr.
TaF_5	4.74	96.8	229.5	c	sol. hydr.
Tellurium					
Te	6.24	452	1390	gy	not sol.
H_2TeO_3	3.05	dec. 40		c	sl. sol.
H_2TeO_4	3.44	d. 160		c	2 aq. 28.9(18°)
H_6TeO_6	3.05			c	sol.
TeO_2	5.89		s. 450	y	giv. H_2TeO_3
TeO_3	5.08				
	(10.5)	d.		c	giv. H_2TeO_4
$TeBr_2$		ca. 280	339	gy	hydr.
$TeCl_2$		175	324	bk	hydr. to TeO
$TeCl_4$		214	414	w	hydr.
TeF_6			− 35.5	c	hydr.
TeI_2				bk	hydr. to TeO
TeI_4	8.40	259		d–br	hydr. slowly
Thallium					
Tl	11.85	303.5	1650	bl–w	not sol.
Tl_2O		300		bk	giv. TlOH
Tl_2O_3	br. 9.65			br	
	bk. 10.19	759		bk	v. sl. sol.
TlOH			139 diss.	y	343 g./liter 18.5°
$Tl(OH)_3$		> 340		br	v. sl. sol.
TlBr	7.56	460	815	l–y	0.05(20°)
$TlBrO_3$				c	0.35(20°)
Tl_2CO_3	7.11			c	3.8(15°), 20(100°)
TlCl	7.00	430		c	0.34(20°), 1.9(90°)
$TlClO_4$	4.89	501		c	17(30°)
TlF			300	c	44(15°)
TlI	7.09	440	824	y	0.0064(20°), 0.1(100°)
TlN_3		334		y	v. sl. sol.
$TlNO_3$	5.55	206	430	c	3.8(0°), 23.3(50°)
$(NH_4)_3TlCl_6 \cdot 2H_2O$	2.39			c	sol.
Tl_3PO_4	6.89			c	0.5(15°)
$Tl_4P_2O_7$	6.79	> 120		c	sl. sol.

Table of Densities, Melting Points, etc. (Cont'd)

Formula	Density	Melting Point °C	Boiling Point °C	Color	Solubility in Water
Tl_2S	8.0	448		bl–bk	0.02(20°)
Tl_2SO_4		632		c	4.64(20°), 15.6(100°)
Tl_2Se		340		gy	sl. sol.
Thorium					
Th	11.2	1845	> 3000	gy	evol. H_2
ThO_2	9.69	> 2800		c	v. sl. sol.
$Th(OH)_4$		d.		c	v. sl. sol.
$ThBr_4$	5.67		s. 610	c	v. sol.
$ThCl_4$	4.59	820		c	v. sol.
$Th_3(PO_3)_4$	4.08			c	sl. sol.
ThS_2	6.8	d.		y	v. sl. sol.
$Th(SO_4)_2 \cdot 9H_2O$	2.77	d.			1.36(20°)
$ThO_2 \cdot SiO_2$	5.3			c	v. sl. sol.
$K_2ThF_6 \cdot H_2O$				c	6×10^{-5}(25°)
Tin					
Sn	w. 7.31 gy. 5.75	231.8	2260	w	not sol.
H_2SnO_3				c	v. sl. sol.
$H_{10}Sn_5O_{15}$					v. sl. sol.
$H_2SnCl_6 \cdot 6H_2O$	1.93			c	sol.
SnO	6.95			bk & d–gr	v. sl. sol.
SnO_2	7.0			gy–w	v. sl. sol.
$Sn(OH)_2$				w y–br	1.6×10^{-4}(25°)
$SnBr_2$	5.12	215.5	620	y	sol.
$SnBr_4$	l. 3.34	31.0	202	c	hydr.
$SnCl_2$		246.8	623	c	
$SnCl_2 \cdot 2H_2O$	2.7	37.7	d.	c	70.1(25°)
$SnCl_4$	l. 2.23	− 30.2	114.1	c	sol. hydr.
SnI_2		320	720	r	0.77(20°), 3.9(100°)
SnI_4	4.46	143.5	340	r–y	hydr.
SnS	5.08	880	1230	br	0.000001(18°)
SnS_2	4.5			y	0.00001(18°)
$SnSO_4$				c	16(20°)
$Sn(SO_4)_2 \cdot 2H_2O$				c	sol. hydr.
Titanium					
Ti	4.5	1800	> 3000	gy	not sol.
TiO				bl–bk	giv. $Ti(OH)_2$
Ti_2O_3	4.6			vi	v. sl. sol.
TiO_2 (Rutile)	4.26	d. 1640		bl	v. sl. sol.
$TiO_2 \cdot 2H_2O$		d.		w	v. sl. sol.
$TiBr_4$		39	230	y	sol. hydr.
$TiCl_2$				bk	sol.
$TiCl_3$		d. 440		v	sol.
$TiCl_4$	1.7	− 30	136	l–y	sol. hydr.
TiN	5.18	2930		br–r	not sol.
TiS_2				gr	hydr. slowly
Tungsten					
W	19.3	3370	5900	gy–bk	not sol.
H_2WO_4	5.5			y	v. sl. sol.
WO_2	12.11			br	v. sl. sol.
WO_3	7.16	1473		y	v. sl. sol.
WC	15.7	2777	6000	gy	not sol.
W_2C	16.06	2877	6000	gr	not sol.
WCl_2				gy	sol. hydr.
WCl_4		d.		gy	sol. hydr. to WO_2
WCl_5		248	275.6	bk	sol.
WCl_6		275	346.7	d–bl	hydr. to WO_3
WBr_5		276	333	d–br	sol.

Table of Densities, Melting Points, etc. (Cont'd)

Formula	Density	Melting Point °C	Boiling Point °C	Color	Solubility in Water
WI_2	6.9			br	hydr.
WI_4	5.2			bk	sol. hydr. to WO_2
WS_2	7.5		gy	gy	not sol.
Uranium					
U	18.7	< 1850		w	evol. H_2
UO_2	10.5			bk	v. sl. sol.
UO_3	5.92			y	v. sl. sol.
U_3O_8	7.31			gr	v. sl. sol.
UBr_4	4.84			bk	v. sol.
UC_2	11.3	2260	4100	gy	giv. UO_2 + hyd-carbn.
U_3N_4				y	hydr.
UCl_4				gr	sol.
UF_6	4.68		s. 56	y	sol. hydr.
UI_4	5.6	500		bk	sol.
$UO_2(IO_3)_2$	5.2	d. 250		y	0.12(18°)
US_2		> 1100		gy	v. sl. sol.
$U(SO_4)_2 \cdot 4H_2O$		4 aq., 300		gr	9.8(24°)
$UO_2(C_2H_3O_2)_2 \cdot 2H_2O$	2.89	d. 275		y	sol.
$UO_2(NO_3)_2 \cdot 6H_2O$	2.74	59	118	y	57(25°)
$UO_2(HPO_4)_2 \cdot 4H_2O$				y	not sol.
UO_2S		d.		br	sl. sol.
$UO_2SO_4 \cdot 3H_2O$	3.28	d. 100		y	14.8(15.5°)
Vanadium					
V	5.96	1710	3000	l–gy	not sol.
HVO_3				y	sl. sol.
$H_4V_2O_7$				br	sl. sol.
VO	5.76			gr	v. sl. sol.
VO_2	4.40	> 1755		d–gr	v. sl. sol.
V_2O_3	4.87	1970		bk	v. sl. sol.
V_2O_5	3.56	800		or & y	giv. HVO_3
VC	5.4	2830	5900	gy	not sol.
VCl_2	3.23			gr	sol.
VCl_3	3.00			pk	sol.
VCl_4	l. 1.82	− 109	148.5	r	sol. giv. $VOCl_2$
VF_4	2.97	d. 325			hydr.
VN	5.63	2050		gr–br	not sol.
V_2S_3	4.7			bk	v. sl. sol.
V_2S_5	3.000			bk	v. sl. sol.
$(VO)(SO_4)$				bl	v. sol.
V_2Si	5.48			w	not sol.
Xenon					
Xe	2.7	− 140	− 109.1	c	21.8 cc./100 cc. H_2O(0°)
Ytterbium					
Yb					evol. H_2
Yb_2O_2	9.17			c	v. sl. sol.
$YbCl_3 \cdot 6H_2O$	2.57			gr	v. sol.
$Yb_2(SO_4)_3$	3.79			c	8 aq. 30.7(0°), 4.5(100°)
$Yb_2(C_2O_4)_3 \cdot 10H_2O$				c	0.000033(25°)
Yttrium					
Y	5.57	1490	2500	gy–bl	evol. H_2
Y_2O_3	4.84	2410		c	v. sl. sol.
$Y(OH)_3$		d.		y	v. sl. sol.
$YCl_3 \cdot H_2O$		160		c	6 aq. 43(25°)
$Y(NO_3)_3 \cdot 6H_2O$	2.68			c	57.4(22.5°)
$Y_2(SO_4)_3 \cdot 8H_2O$	2.56			c	aq. 6.7(25°)
Zinc					
Zn	7.14	419.43	907	gy	not sol.
ZnO	5.47			w	0.0042(18°)
$Zn(OH)_2$	3.053	d. 125		c	v. sl. sol.
$Zn(C_2H_3O_2) \cdot 2H_2O$	1.73	237		c	23.7(20°)

Table of Densities, Melting Points, etc. (Cont'd)

Formula	Density	Melting Point °C	Boiling Point °C	Color	Solubility in Water
$ZnBr_2$	4.22	394	650	c	82.5(25°)
$ZnCO_3$	4.44	d. 300		c	0.001(25°)
$ZnCl_2$	2.91	365	732	c	78.6(20°)
$ZnCl_2 \cdot 2NH_3$		210.8	d. 271	c	giv. $Zn(NH_3)_4^{++}$
$Zn(ClO_3)_2 \cdot 4H_2O$	2.15			c	67.6(30°)
$Zn(ClO_4)_2 \cdot 6H_2O$	2.15			c	v. sol.
$Zn(CN)_2$		d. 800		c	sol.
$Zn_2Fe(CN)_6 \cdot 3H_2O$			d.	c	v. sl. sol.
ZnF_2	4.84	872		c	1.6(18°)
ZnI_2	4.66	446	624	c	83.1(22°)
$Zn(IO_3)_2$	4.98	d.		c	0.87 in "cold" H_2O
$Zn(NO_3)_2 \cdot 6H_2O$	2.06	36.4		c	55.9(25°)
$ZnC_2O_4 \cdot 2H_2O$	2.56	d. 100		c	0.0007(25°)
Zn_3P_2	4.55	> 420	1100	gy	not sol. giv. PH_3 with H^+
$Zn_3(PO_4)_2$	3.998	900		c	v. sl. sol.
$Zn_2P_2O_7$				c	v. ls. sol.
ZnS (α)	4.08	1850 (150 atm.)	s. 1185	c	0.0007(18°)
$ZnSO_4$	3.74	d. 740		c	
$ZnSO_4 \cdot 7H_2O$	1.97		d. 280	c	36.7(25°)
$ZnO \cdot SiO_2$	3.52	1437		c	v. sl. sol.
ZnTe	5.54	1238.5		r	v. sl. sol.
Zirconium					
Zr	6.4	1700	> 2900	gy	not sol.
ZrO_2	5.49	2700		w	v. sl. sol.
$Zr(OH)_4$	3.25	2 aq. 550		w	0.02
$ZrCl_4$				c	sol. hydr.
ZrF_4	4.43	d.		c	sol. hydr.
$Zr(NH_4)_3F_7$				c	sl. sol.
$Zr(NO_3)_4 \cdot 5H_2O$		d. 100		c	sol.
$Zr(SO_4)_2 \cdot 4H_2O$				c	146(39.5°)
ZrO_2SiO_2	4.5	2500		c	v. sl. sol.

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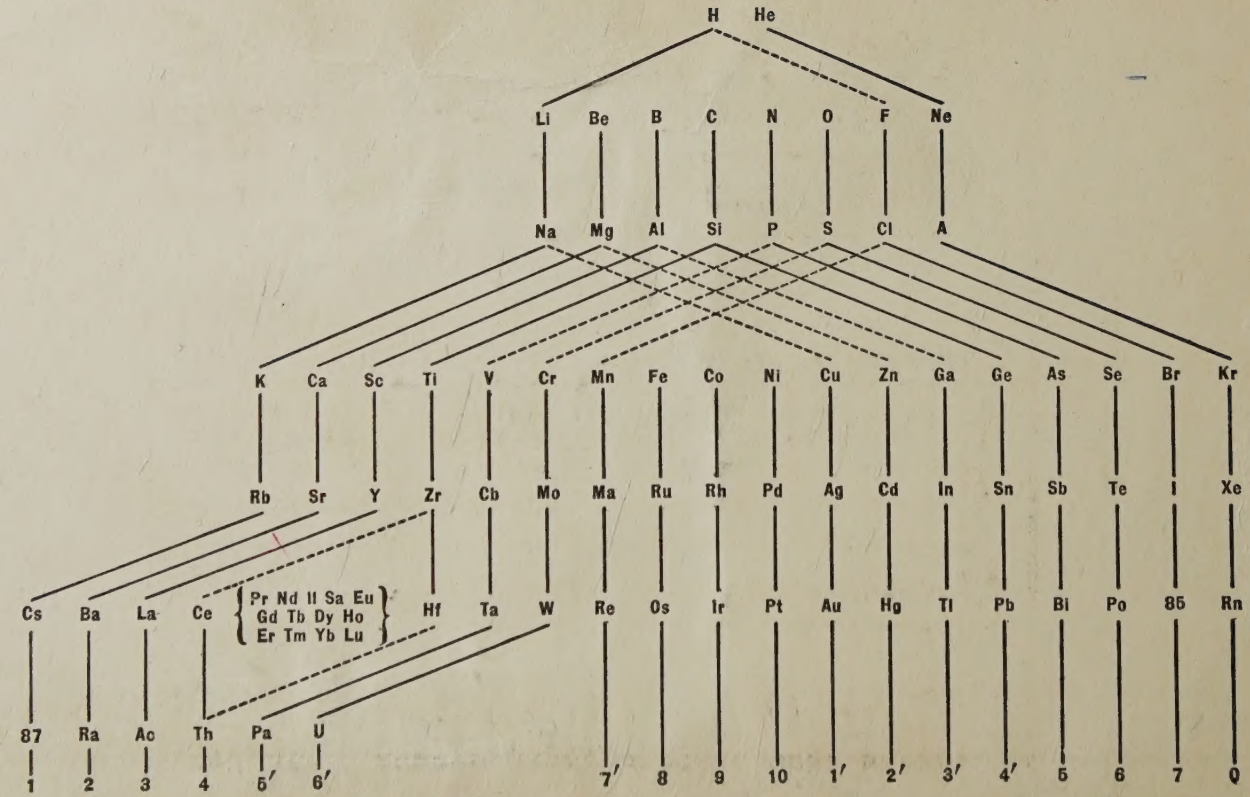
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